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# UNIT M

## electrochemistry

How low a state will  
they reduce themselves too??!



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## UNIT M - ELECTROCHEMISTRY

### OBJECTIVES

After studying Unit M - Electrochemistry the student should be able to:

- M1. Define and use the terms; reduction, oxidation, oxidizing agent, and reducing agent.
- M2. Use experimental data to rank oxidizing agents and reducing agents in order of strength.
- M3. Write half reactions for redox reactions.
- M4. Use reduction potential tables to predict the most likely redox reaction in a given chemical system, to balance the net ionic equation for the reaction, and to determine whether or not the reaction is spontaneous (in terms of strengths of oxidizing agents and  $E^\circ$  values).
- M5. Do stoichiometric calculations based on spontaneous redox reactions.
- M6. Calculate the concentration of solutions from redox titration data.
- M7. Completely analyze an electrochemical cell, giving the anode and cathode reactions, the cell voltage, and the direction of ion and electron flow.
- M8. Define, use and calculate the electrical quantities; charge, current, potential difference and energy.
- M9. Completely analyze an electrolytic cell, giving the anode and cathode reactions, and the minimum cell voltage required.
- M10. Do stoichiometric calculations based on electrolytic cells.
- M11. Use proper titration techniques.
- M12. Construct electrochemical and electrolytic cells.
- M13. Recognize the importance of electrochemistry in consumer chemistry, environmental chemistry, industrial chemistry and historical chemistry.
- M14. Recognize that redox reactions are all stoichiometric but that their rates of reaction may vary considerably.



## AN INTRODUCTION TO REDOX - LAB M1

Purpose:

1. To determine experimentally whether or not a reaction occurs when certain metals are placed in aqueous solutions containing certain metallic ions.
2. To compare the relative tendencies of metals to react with metallic ions in aqueous solution and conversely to compare the relative tendencies of metallic ions in aqueous solution to react with metals.

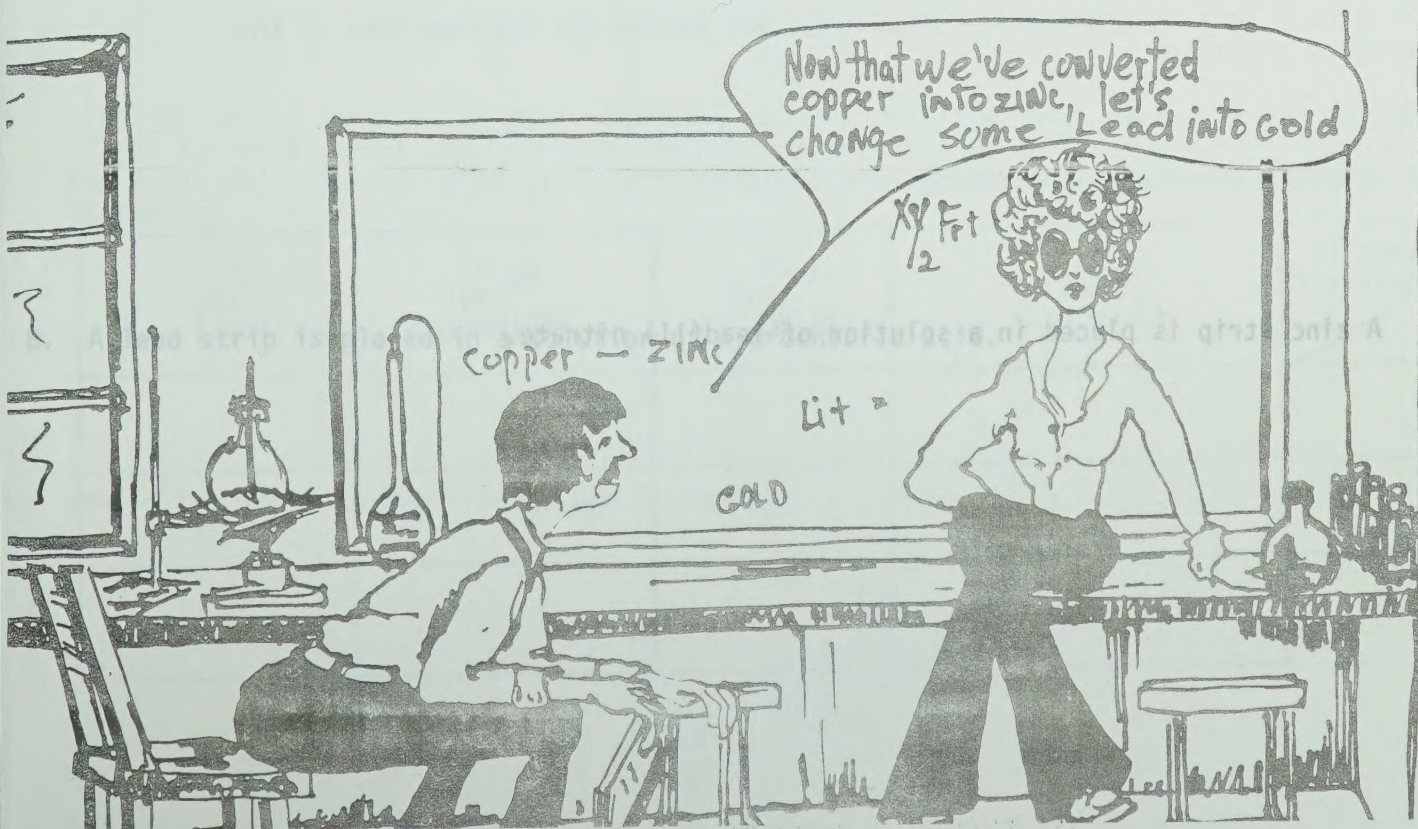
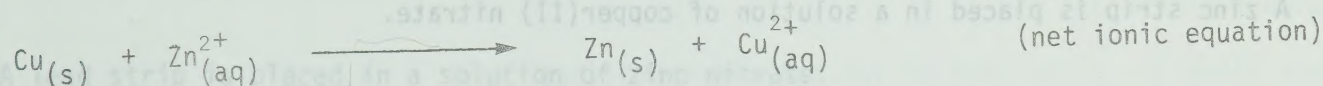
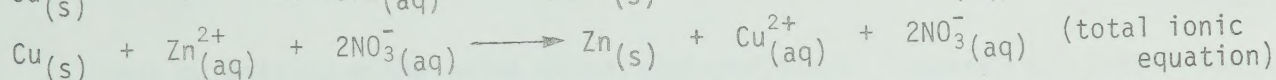
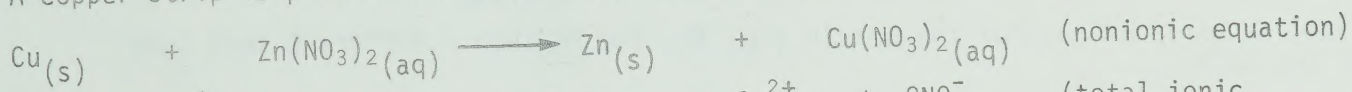
Prelab Exercise:

Chemical reactions which occur on their own, without the input of additional energy, are termed *spontaneous*. In this lab it is determined experimentally whether certain single replacement reactions are spontaneous or not spontaneous. In each of the following situations write balanced equations to represent the reaction expected. All the metal strips are free of oxides and all the solutions are aqueous. For each case write:

1. the nonionic equation
2. the total ionic equation
3. the net ionic equation.

Example:

A copper strip is placed in a solution of zinc nitrate





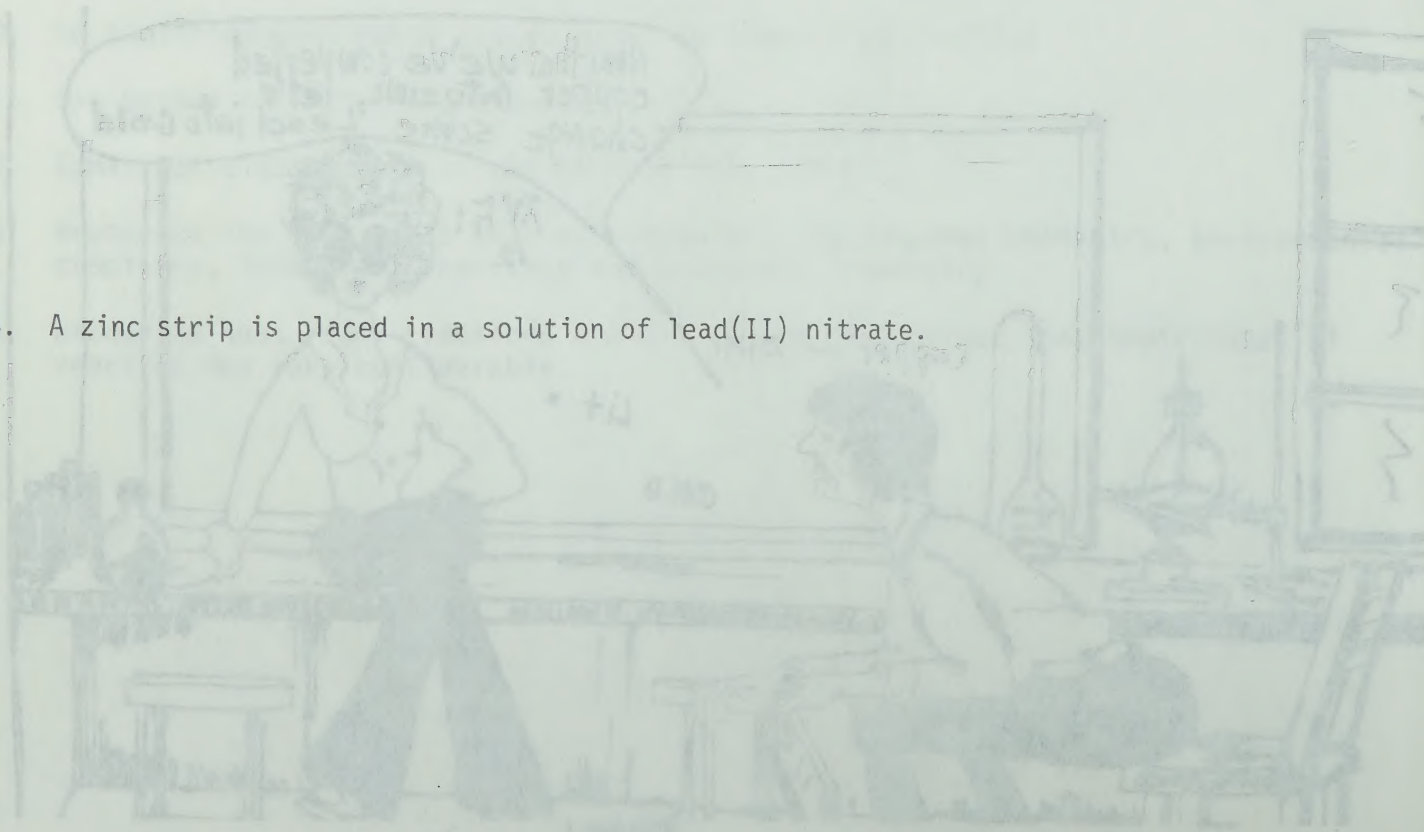
## AN INTRODUCTION TO REDOX - LAB M1

1. A copper strip is placed in a solution of lead(II) nitrate.

2. A copper strip is placed in a solution of hydrochloric acid.

3. A zinc strip is placed in a solution of copper(II) nitrate.

4. A zinc strip is placed in a solution of lead(II) nitrate.





## ELECTROCHEMISTRY

## AN INTRODUCTION TO REDOX - LAB M1

5. A zinc strip is placed in a solution of hydrochloric acid.
6. A lead strip is placed in a solution of copper(II) nitrate.
7. A lead strip is placed in a solution of zinc nitrate.
8. A lead strip is placed in a solution of hydrochloric acid.

## ELECTROCHEMISTRY

## AN INTRODUCTION TO REDOX - LAB M1

Materials:

- |  |  |
|--|--|
| 12 - clean 13 x 100 mm test tubes  | 15 ml of 1.0 M $\text{Cu}(\text{NO}_3)_2(\text{aq})$ |
| 4 - 4 x 100 mm (approx.) strips of each of metals - copper, zinc, and lead | 15 ml of 1.0 M $\text{Zn}(\text{NO}_3)_2(\text{aq})$ |
| 4 - 50 ml beakers  | 15 ml of 1.0 M $\text{Pb}(\text{NO}_3)_2(\text{aq})$ |
| - sand paper or steel wool   | 15 ml of 1.0 M $\text{HCl}(\text{aq})$               |

Procedure:

- Use labeled 50 ml beakers to obtain 15 ml of each of the 1.0 M solutions -  $\text{Cu}(\text{NO}_3)_2(\text{aq})$ ,  $\text{Zn}(\text{NO}_3)_2(\text{aq})$ ,  $\text{Pb}(\text{NO}_3)_2(\text{aq})$ ,  $\text{HCl}(\text{aq})$ .
- Clean the surface of each metal strip with sand paper or steel wool to remove any surface coatings.
- Half fill each of 3 test tubes with the 1.0 M  $\text{Cu}(\text{NO}_3)_2(\text{aq})$  solution.
- Place on strip of each of the metals (Cu, Zn, and Pb) into a different test tube of the  $\text{Cu}(\text{NO}_3)_2$ .
- Observe and record any changes. Place the test tubes aside while setting up the remainder of the lab.
- Repeat Steps 2 - 4 for each of the solutions provided.
- Observe each test tube after 5 - 10 minutes and record the observations in the data chart provided.

Observations:

List any evidence for a chemical change.

Species in Metal Strips \ Solution	$\text{Cu}^{2+}_{(\text{aq})}$ ( $\text{Cu}(\text{NO}_3)_2$ )	$\text{Zn}^{2+}_{(\text{aq})}$ ( $\text{Zn}(\text{NO}_3)_2$ )	$\text{Pb}^{2+}_{(\text{aq})}$ ( $\text{Pb}(\text{NO}_3)_2$ )	$\text{H}^{+}_{(\text{aq})}$ ( $\text{HCl}$ )
$\text{Cu}_{(\text{s})}$				
$\text{Zn}_{(\text{s})}$				
$\text{Pb}_{(\text{s})}$				



## AN INTRODUCTION TO REDOX - LAB M1

Questions:

1. Go back to the equations in the Prelab Exercise and indicate which reactions are spontaneous and which are not spontaneous by writing *spont* or *not spont* on the arrow of the net ionic equation.
2. What generalization can be made about the reaction between a metal and its own aqueous ion?
3. If the forward reaction is spontaneous will the reverse reaction also be spontaneous?
4. List the metallic ions in order of their tendency to form metals, from greatest to least. (Place the ion which reacted with the most different metals at the top of the list and the ion which reacted with the least different metals at the bottom of the list.)
5. List the metals in order of their tendency to form positive ions, from greatest to least. (Place the metal which reacted with the most different ions at the top of the list and the metal which reacted with the least different ions at the bottom of the list.) Include  $\text{H}_2(\text{g})$  in the list.
6. How do the lists in Questions 5 and 6 compare?

## INTRODUCTION

Many chemical reactions involve the release of the energy stored in chemical bonds directly as electricity. The spontaneous reactions which occur in flashlight batteries and car batteries are examples. Other chemical reactions require the direct input of electricity to store more energy in chemical bonds. Many metals are produced in this way.

From the Lab M1, it is evident that metals can change to ions and metallic ions can change to free metals. Consider the net equation written below.



Copper ions, with a net charge of 2+, have changed to copper atoms, with a net charge of zero. In order for this to happen each copper ion must gain two electrons.



Zinc atoms, with no net charge, have changed to zinc ions with a charge of 2+. In order for this to happen each zinc atom must lose two electrons.



Overall, each copper ion has removed two electrons from each zinc atom.

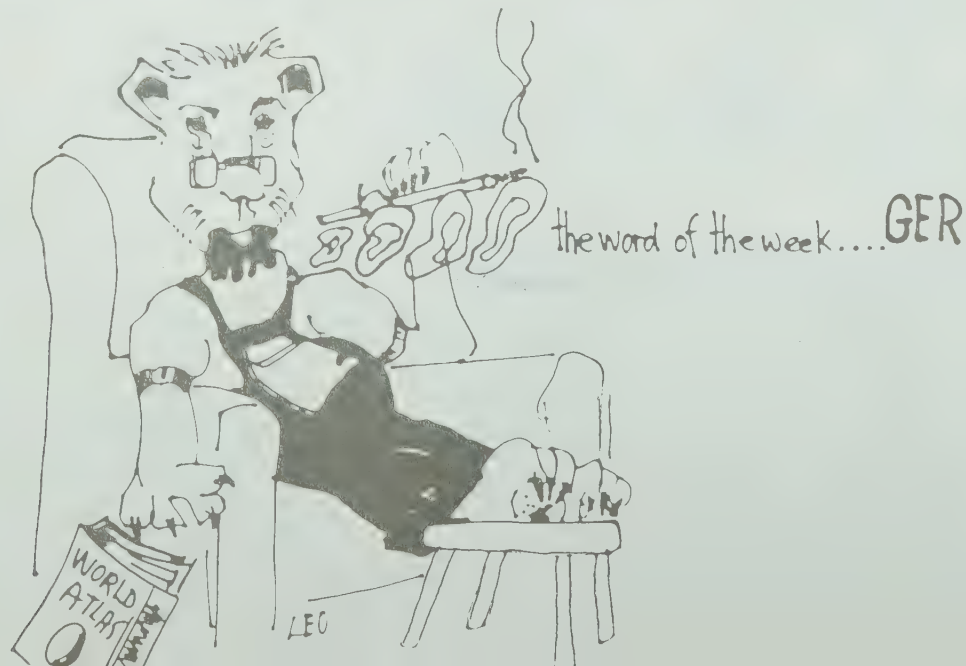
Any such reaction which involves a transfer of electrons can be written as two separate equations, one expressing the loss of electrons and one expressing the gain of electrons. For every reaction of this type electrons are conserved; i.e., the number of electrons gained equals the number of electrons lost.

A reaction involving either a gain or a loss of electrons with the electrons written in the equation is called a *half reaction*. Two such *half reactions* make up a total reaction. The half reaction which involves a gain of electrons is called a *reduction* half reaction. The half reaction which involves a loss of electrons is called an *oxidation* half reaction. The combined total reaction is called a *reduction-oxidation* reaction (*redox reaction*).

Definitions:

*Oxidation* - a chemical change involving a loss of electrons. (L.E.O.)

*Reduction* - a chemical change involving a gain of electrons. (G.E.R.)

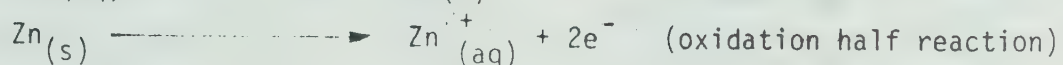
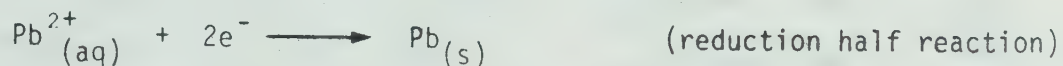




# WRITING HALF REACTIONS FROM A NET REACTION

The following balanced net ionic equations represent spontaneous chemical reactions from Lab M1. For each case write the half reactions and indicate which is the reduction half reaction and which is the oxidation half reaction.

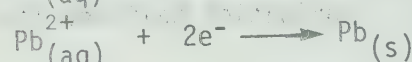
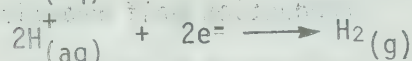
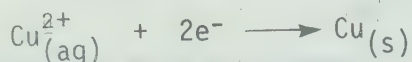
Example:



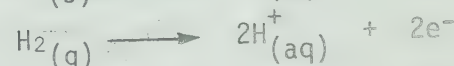
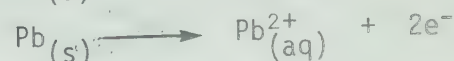
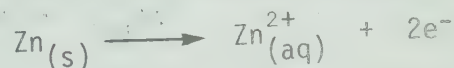
## HALF REACTION TABLES

In Questions 5 and 6 of Lab M1 the metals and ions used in the lab were listed in order of their tendency to react. These lists can be written as reduction and oxidation half reactions

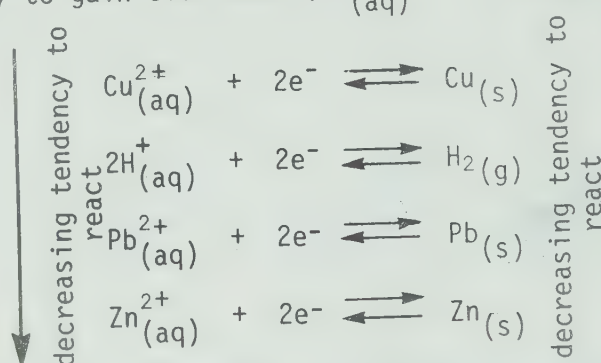
## Reaction of Ions in Lab M1



## Reaction of Metals in Lab M1



Notice that the first list is ordered from copper to zinc and the second list is ordered from zinc to copper. The metal ion with the greatest tendency to gain electrons ( $\text{Cu}^{2+}_{(\text{aq})}$ ) reacts to produce the metal with the least tendency to lose electrons ( $\text{Cu}_{(\text{s})}$ ). The metal with the greatest tendency to lose electrons ( $\text{Zn}_{(\text{s})}$ ) reacts to produce the metal ion with the least tendency to gain electrons ( $\text{Zn}^{2+}_{(\text{aq})}$ ). The two lists above may be combined into one list.



The above list expanded to contain many other half reactions is included in the *ALCHEM data sheet*. The table on the data sheet is named the *Reduction Potential Table*. The substance which has the greatest tendency to gain electrons,  $\text{F}_2$ , is written at the top of the *Reduction Potential Table*.  $\text{F}_2$  reacts to produce the  $\text{F}^{-}$  ion. The  $\text{F}^{-}$  ion has the strongest attraction for electrons and is therefore the most difficult to oxidize.

The substance which has the least tendency to gain electrons,  $\text{Li}^{+}$ , is written at the bottom of the *Reduction Potential Table*.  $\text{Li}^{+}$  reacts to produce the  $\text{Li}$  atom. The  $\text{Li}$  atom has the least attraction for its electrons and is therefore the easiest to oxidize.



# ELECTROCHEMISTRY

## REDUCTION POTENTIAL TABLE

### Definitions:

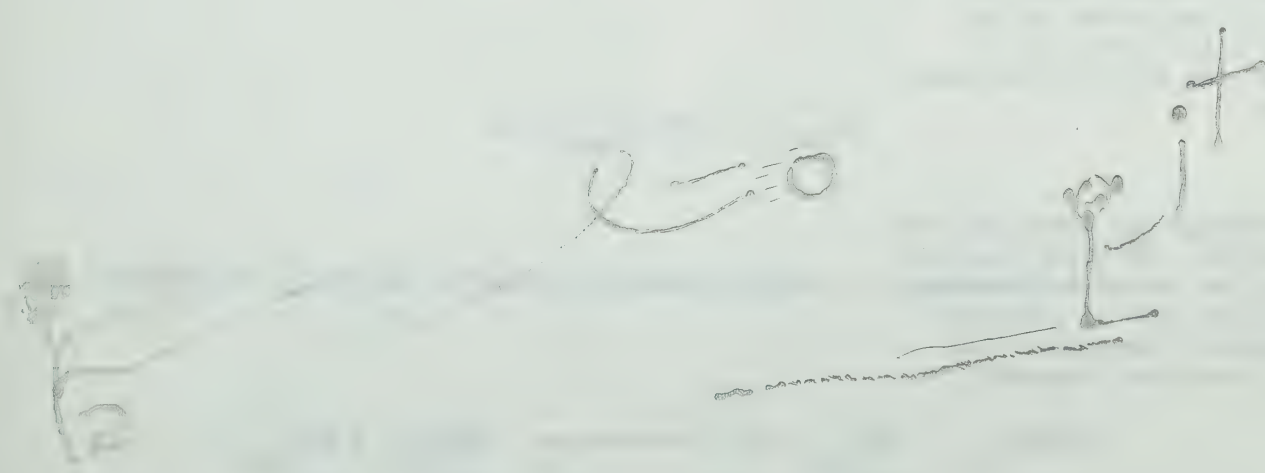
An oxidizing agent removes electrons from another substance; i.e., oxidizes it. An oxidizing agent itself gains electrons and becomes reduced.

A reducing agent gives up electrons to another substance; i.e., reduces it. A reducing agent itself loses electrons and becomes oxidized.

The left side of the reduction potential table can be considered as a list of oxidizing agents in order of strength, with the strongest oxidizing agent at the top and the weakest at the bottom. Remember that the substances on the left are listed in order of their tendency to *gain* electrons. Similarly the right side of the reduction potential table can be considered as a list of reducing agents in reverse order of strength with the strongest reducing agent at the bottom and the weakest at the top.

### Reduction Potential Table

Strongest Oxidizing Agent (S.O.A.). Easiest to Reduce	$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	Weakest Reducing Agent. Most Difficult to Oxidize
Weakest Oxidizing Agent Most Difficult to Reduce	$Li^+(aq) + e^- \rightleftharpoons Li(s)$	Strongest Reducing Agent (S.R.A.). Easiest to Oxidize



## USING THE REDUCTION POTENTIAL TABLE

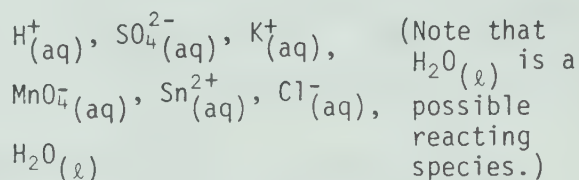
The reduction potential table can be used to predict possible redox reactions in a given chemical system, to write balanced net ionic equations for the reactions, and to determine whether or not the reaction will be spontaneous.

Example:

Predict the most likely redox reaction to occur when sulfuric acid, and aqueous solutions of potassium permanganate and tin(II) chloride are mixed together in the same beaker. Balance the equation for the reaction and determine whether or not it will be spontaneous.

Step 1:

List all the chemical species present in the solution. Assume all ionic compounds are completely dissociated in aqueous solution.

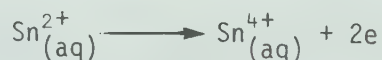
Step 2:

Use the reduction potential table to identify the strongest oxidizing agent (S.O.A.) and write its half reaction.

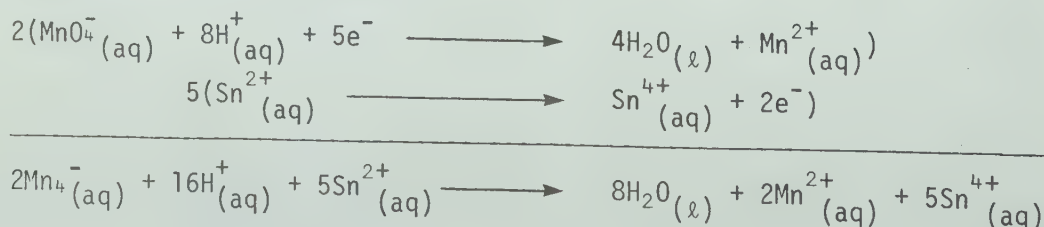
(Note: The  $\text{MnO}_4^-_{(\text{aq})}$  ion requires  $\text{H}^+_{(\text{aq})}$  when it acts as an oxidizing agent.)

Step 3:

Use the reduction potential table to identify the strongest reducing agent (S.R.A.) and write its half reaction. The half reaction is reversed from the way it is written in the table.

Step 4:

Write the balanced net ionic equation for the reaction. Multiply the half reactions by the smallest whole numbers to make the gain of electrons equal the loss of electrons, then add the half reactions together.





2. Bromine gas is bubbled through an aqueous solution of sodium chloride.

## ELECTROCHEMISTRY

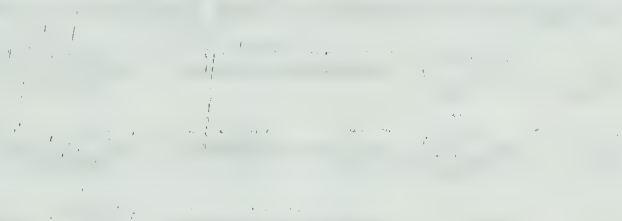
## USING THE REDUCTION POTENTIAL TABLE

3. A strip of silver is placed into an aqueous solution of chromium(III) nitrate.
4. Hydrochloric acid is added to an aqueous solution of potassium dichromate.
5. An iron wire is placed in an aqueous solution of magnesium chloride.

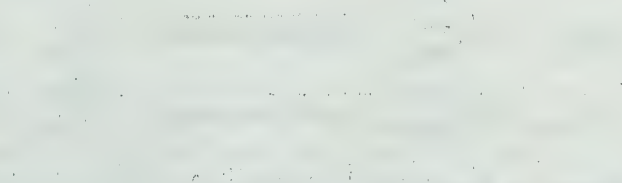


## USING THE REDUCTION POTENTIAL TABLE

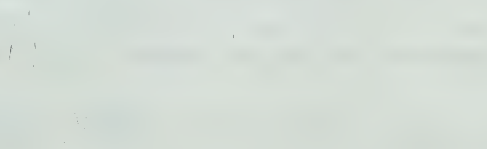
6. A copper wire is placed in a solution of hydrochloric acid.



7. A copper wire is placed in a solution of nitric acid.



8. An iron bolt is exposed to moist air.



## ELECTROCHEMISTRY

## USING THE REDUCTION POTENTIAL TABLE

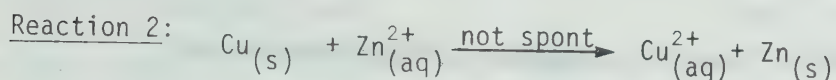
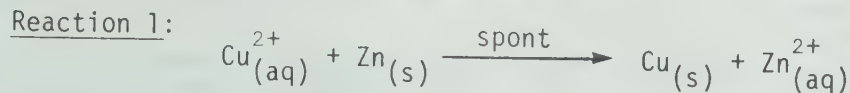
9. Determine whether the following reactions will be spontaneous or not spontaneous. Write *spont* or *not spont* on the arrow of the equation to indicate the prediction.



10. How do the predictions in Question 9 compare with the results of Lab M1?

## EQUILIBRIUM IN REDOX REACTIONS

In Lab M1 it was noted that when a particular redox reaction was spontaneous, the reverse reaction was not spontaneous; e.g.,



These results may be explained in terms of equilibrium.

*Equilibrium* is recognized in a closed chemical system when the observable properties of the system (e.g., color, temperature, amount of solid phase) remain constant even though some of the reactants remain in the system. Although it appears that all chemical change has stopped in equilibrium systems, careful experiments show that chemical changes do continue. In equilibrium systems the rates of two opposing reactions are equal to each other so that no net change occurs in the system. For example, in a closed chemical system atoms of A and B combine to form molecules of C. As molecules of C are formed some of them decompose to form atoms of A and B. When the two opposite reactions proceed at the same rate the system has reached equilibrium. This equilibrium system may be represented in equation form as:



In Reaction 1 above, the system did not reach equilibrium until the concentration of products was much greater than the concentration of the reactants. In Reaction 2 (the reverse reaction) equilibrium was reached when the concentration of the reactants was much higher than the concentration of products. These equilibrium conditions are so extreme that we can conveniently say that Reaction 1 went to completion and Reaction 2 did not occur appreciably.

Usually, redox reactions either go to completion (spontaneous) or do not occur appreciably (not spontaneous). Redox reactions which reach equilibrium with roughly equal concentrations of products and reactants are quite rare. This means that the quantities of reactants which will be required for a given redox reaction can be calculated from the balanced chemical equation for the reaction. These stoichiometric calculations are quite useful for determining the concentrations of aqueous solutions from titration data.

Although the spontaneity of a redox reaction can be predicted from reduction potential tables, there is no simple way of predicting the *rate* of a redox reaction. Reactions involving the production of gases are generally slow and the production of oxygen is particularly slow. Titration experiments are only practical with reasonably rapid reactions. It is also helpful in redox titrations if one of the reacting species undergoes a color change during the reaction. This color change can be used to indicate the end point of the reaction. Two commonly used oxidizing agents which undergo color change are acidic dichromate ions and acidic permanganate ions.





ELECTROCHEMISTRY  
REDOX TITRATION - LAB M2

Purpose:

Part A:

1. To prepare a standard solution of iron(II) ammonium sulfate hexahydrate ( $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ).
2. To determine the molar concentration of an aqueous potassium permanganate solution.

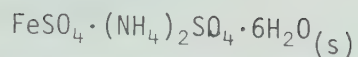
## Part B:

3. To determine the percentage of iron in a mixture that contains an iron(II) salt and inert substances.

### Prelab Exercise:

- Prelab Exercise:
1. Write the balanced net ionic equation for the reaction of  $\text{Fe}^{2+}_{(\text{aq})}$  and  $\text{MnO}_4^{-}_{(\text{aq})}$  in acidic solution.
  2. Calculate the mass of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  required to make 100 ml of 0.050 M solution.

## REDOX TITRATION - LAB M2

Materials:

- 1 - 100 ml beaker
- 1 - 100 ml volumetric flask
- 2 - 250 ml Erlenmeyer flask
- 1 - stopper for 250 ml Erlenmeyer
- 1 - 50 ml buret
- 1 - 25 ml pipet

- 1 - pipet bulb
- 1 - stirring rod
- 1 - 10 ml graduated cylinder
- 1 - short stemmed funnel
- $\text{KMnO}_4$  of unknown concentration
- stock solution of 3 M  $\text{H}_2\text{SO}_4(\text{aq})$
- sample of iron(II) unknown

Procedure:Part A:

1. Use a balance and a piece of paper to obtain the mass of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}_{(s)}$  determined in the Prelab Exercise.
2. Use the 100 ml beaker to obtain about 40 ml 3 M  $\text{H}_2\text{SO}_4(\text{aq})$
3. Transfer the  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}_{(s)}$  to the beaker containing the 40 ml of 3 M  $\text{H}_2\text{SO}_4(\text{aq})$ . Stir the mixture until all the  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}_{(s)}$  has dissolved.
4. Use the funnel to transfer the  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}_{(aq)}$  solution from the 100 ml beaker to the 100 ml volumetric flask.
5. Dilute the solution to exactly 100 ml and mix thoroughly.
6. Pour the prepared solution into a clean, dry 250 ml Erlenmeyer flask.  
(Do not dilute this solution in any manner.)
7. Set up and rinse the 50 ml buret. Fill the buret with the permanganate solution of unknown concentration. Record the initial buret reading of the permanganate solution to the nearest 0.1 ml.  
(Note: Use the upper edge of the meniscus since the bottom of the meniscus is obscured.)
8. Pipet 25.0 ml of the standard iron(II) solution into another clean 250 ml Erlenmeyer flask.
9. Titrate the sample of iron(II) salt solution with the permanganate solution. Swirl the solution in the Erlenmeyer to ensure complete mixing.  
(When a single drop brings about a faint *persisting* pink tinge in the liquid, the endpoint has been reached.)
10. Record the final buret reading.
11. Repeat Steps 8 - 10 two more times.



## ELECTROCHEMISTRY

## REDOX TITRATION - LAB M2

Part B:

1. Use a clean, dry 100 ml beaker to obtain about 80 ml of the iron(II) solution of unknown concentration. Pour the solution into a clean, dry 250 ml Erlenmeyer flask and stopper the flask.
2. Pipet 25.0 ml of the solution obtained in Step 1 into another clean 250 ml Erlenmeyer flask.
3. Using a graduated cylinder add about 3 ml of 3 M  $\text{H}_2\text{SO}_4(\text{aq})$ .
4. Rinse and fill the buret with potassium permanganate solution. Record the initial buret reading.
5. Titrate the iron(II) solution with the previously standardized permanganate solution. Record the final buret reading.
6. Repeat Steps 2 - 5 two more times.

Observations:Part A: Mass of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  \_\_\_\_\_

	Trial 1	Trial 2	Trial 3
final buret reading			
initial buret reading			
volume of $\text{KMnO}_4(\text{aq})$ used			
average volume of $\text{KMnO}_4(\text{aq})$			

Part B:

	Trial 1	Trial 2	Trial 3
volume of $\text{Fe}^{2+}(\text{aq})$ solution			
final buret reading			
initial buret reading			
volume of $\text{KMnO}_4(\text{aq})$ used			
average volume of $\text{KMnO}_4(\text{aq})$			

REDOX TITRATION - LAB M2

Calculations:

1. Using the balanced equation from the prelab exercise, determine the molarity of the potassium permanganate solution. Use the average volume of  $\text{KMnO}_4(\text{aq})$  used.
2. Use the average volume of  $\text{KMnO}_4(\text{aq})$  used in Part B to determine the concentration of iron(II) ions in the solution used in Part B.
3. Given that 5.00 L of the unknown solution was prepared from 25.0 g of iron ore, calculate the percentage of iron by mass in the ore sample.

Questions:

1. If some of the iron in the unknown solution is in the form of  $\text{Fe}^{3+}(\text{aq})$  ions, how will this effect the calculation of the percentage of iron in the ore?
2. What is the purpose of adding  $\text{H}_2\text{SO}_4(\text{aq})$  to the  $\text{Fe}^{3+}(\text{aq})$  solutions before titrating with  $\text{KMnO}_4(\text{aq})$ ?
3. In the procedure (Part B, Step 1) you were instructed to use a *dry* 250 ml Erlenmeyer flask. Why is it important that the flask be dry? Is it also necessary that the flask used in Step 2 be dry? Explain.

## ELECTROCHEMISTRY

## REDOX STOICHIOMETRY

1. In an experiment similar to Lab M2, 0.0500 M  $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$  was used in an acidic solution to oxidize  $\text{Fe}_{(\text{aq})}^{2+}$  ions to  $\text{Fe}_{(\text{aq})}^{3+}$  ions. The following data were obtained.

volume of $\text{Fe}_{(\text{aq})}^{2+}$ solution	25.0 ml
final buret reading ( $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ )	48.7 ml
initial buret reading	3.7 ml

What was the concentration of the  $\text{Fe}_{(\text{aq})}^{2+}$  ions in the solution?

2. In another experiment similar to Lab M2, the  $\text{Sn}_{(\text{aq})}^{2+}$  ions in an acidic solution were oxidized to  $\text{Sn}_{(\text{aq})}^{4+}$  by a 0.200 M  $\text{KMnO}_4(\text{aq})$  solution. The following data were obtained:

volume of $\text{Sn}_{(\text{aq})}^{2+}$ solution	10.0 ml
final buret reading ( $\text{KMnO}_4(\text{aq})$ )	39.3 ml
initial buret reading	1.8 ml

What was the concentration of  $\text{Sn}_{(\text{aq})}^{2+}$  in the solution?



## ELECTROCHEMISTRY

## REDOX STOICHIOMETRY

3. Copper(II) nitrate can be produced by reacting copper metal with concentrated nitric acid. What volume of 15 M  $\text{HNO}_3(\text{aq})$  is needed to react with 12.7 g of copper?
4. Bromine can be obtained by bubbling chlorine gas through sea water. The concentration of bromide ions in sea water is 0.00800 M. What mass of chlorine gas is needed to oxidize all the bromide ions in 1000 L of water?
5. The copper(II) ions in a solution can be converted to copper metal by trickling the solution over scrap iron. The reaction produces iron(II) ions from the scrap iron. If the process produces 25 L of solution containing 0.0020 mol/L of  $\text{Fe}^{2+}(\text{aq})$  ions, what mass of copper is produced?

## ELECTROCHEMISTRY

## REDOX STOICHIOMETRY

6. In *ALCHEM 20* the concentration of a solution of copper(II) sulfate was determined by placing a zinc strip into a copper(II) sulfate solution. One student obtained the following data:

volume of $\text{CuSO}_4(\text{aq})$	100.0 ml
mass of copper produced	12.7 g

Calculate the concentration of the copper(II) sulfate solution.

7. In an experiment a copper wire was placed in an aqueous solution of silver acetate. The following data were obtained?

volume of $\text{AgCH}_3\text{COO}(\text{aq})$	200 ml
mass of Cu wire before	12.781 g
mass of Cu wire after	12.527 g

Calculate the concentration of the silver acetate solution.

## ELECTROCHEMICAL CELLS

In reduction-oxidation reactions electrons are transferred from the substance oxidized to the substance reduced. The reactants can be arranged so that the electron transfer occurs through a conducting wire. In this arrangement the oxidation half reaction and the reduction half reaction take place in separate containers called *half-cells*. When two half-cells are joined so that a path is provided for the movement of electrons and another path is provided for the movement of positive and negative ions, then electric current will flow through the system. Such an arrangement of half-cells is called an *electrochemical cell*.

Recall that in Lab M1 a spontaneous reaction occurred when a zinc strip was placed in a solution containing  $\text{Cu}^{2+}_{(\text{aq})}$  ions. In the arrangement diagrammed in Figure M1 a zinc strip is placed in a porous cup containing aqueous zinc sulfate and a copper strip is placed in a beaker containing aqueous copper(II) sulfate. In the arrangement shown in Figure M1 no reaction occurs in the half-cells and no current flows in the wire. However, as soon as the porous cup is placed in the beaker current flows through the system.

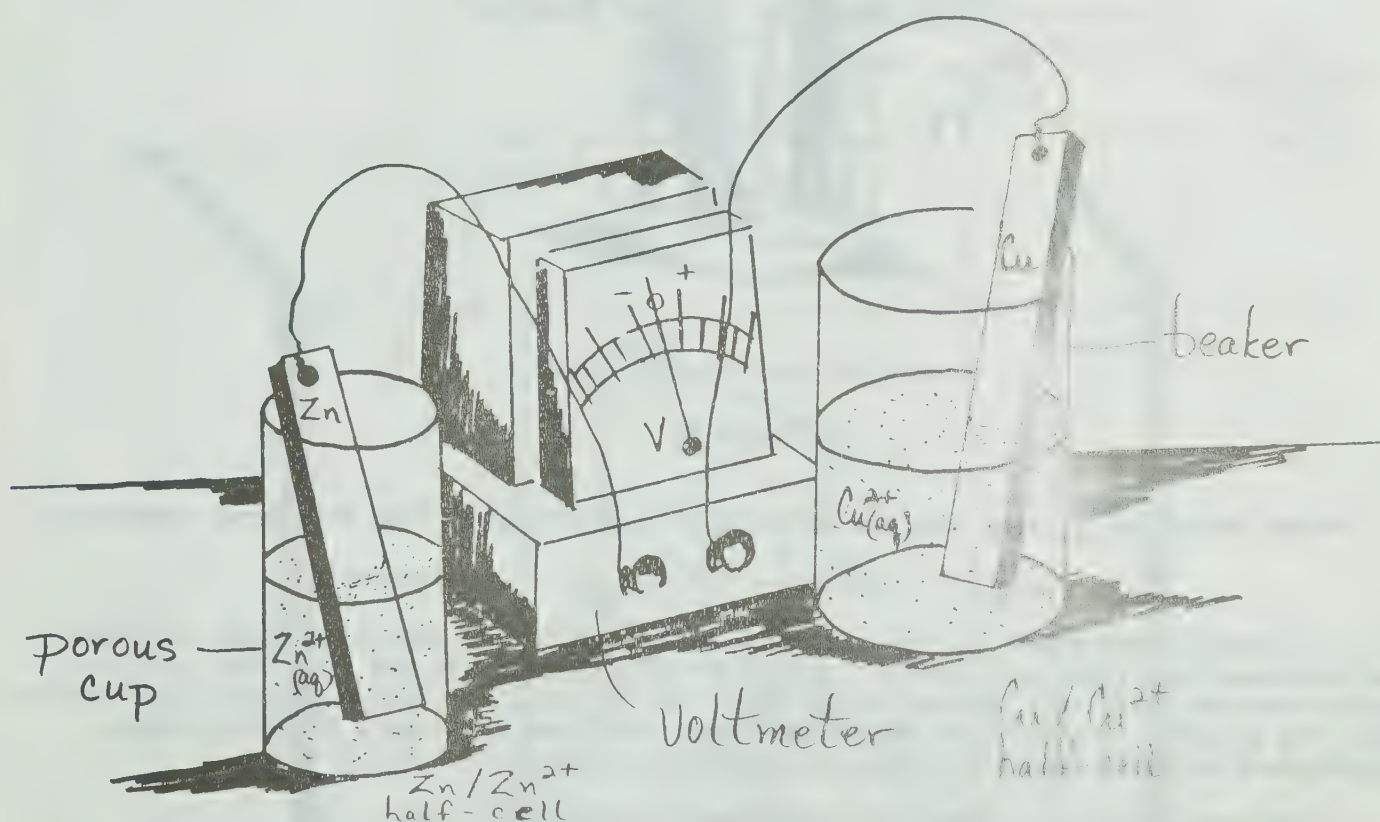


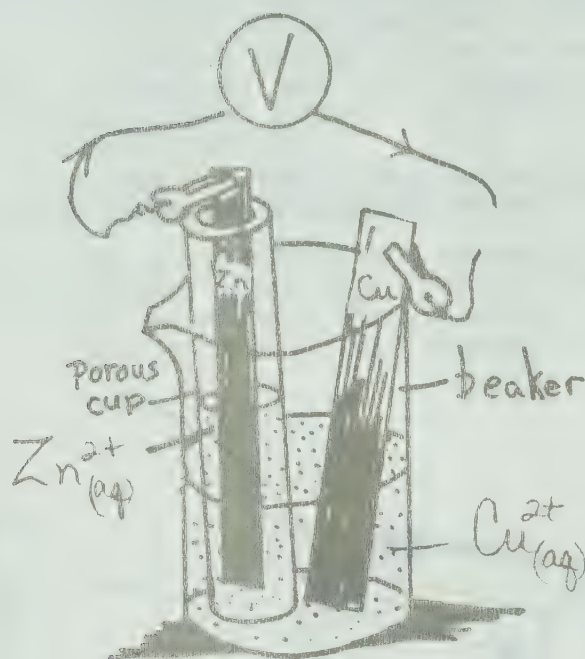
Figure M1

When the porous cup is placed in the beaker (as in Figure M2) chemical reactions proceed in each half-cell. As a result of these reactions electrons flow through the wire and ions migrate through the walls of the porous cup from one half-cell to another.



# ELECTROCHEMISTRY

## ELECTROCHEMICAL CELLS



An Electrochemical Cell

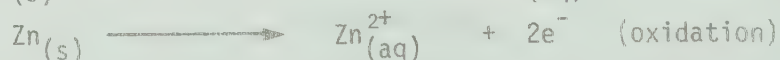
Figure M2

In the beaker  $\text{Cu}_{(\text{aq})}^{2+}$  ions from the solution pick up electrons from the copper electrode.



The  $\text{Cu}_{(\text{s})}$  atoms formed adhere to the copper electrode. This half reaction removes electrons from the copper electrode and leaves it with a positive charge. At the same time, this half reaction removes positively charged  $\text{Cu}_{(\text{aq})}^{2+}$  ions from the solution leaving an excess of negative ions. The solution in the region around the copper electrode acquires a negative charge. The electrode at which reduction occurs is called the cathode. (G.E.R.C.)

In the porous cup  $\text{Zn}_{(\text{s})}$  atoms lose electrons to form  $\text{Zn}_{(\text{aq})}^{2+}$  ions.



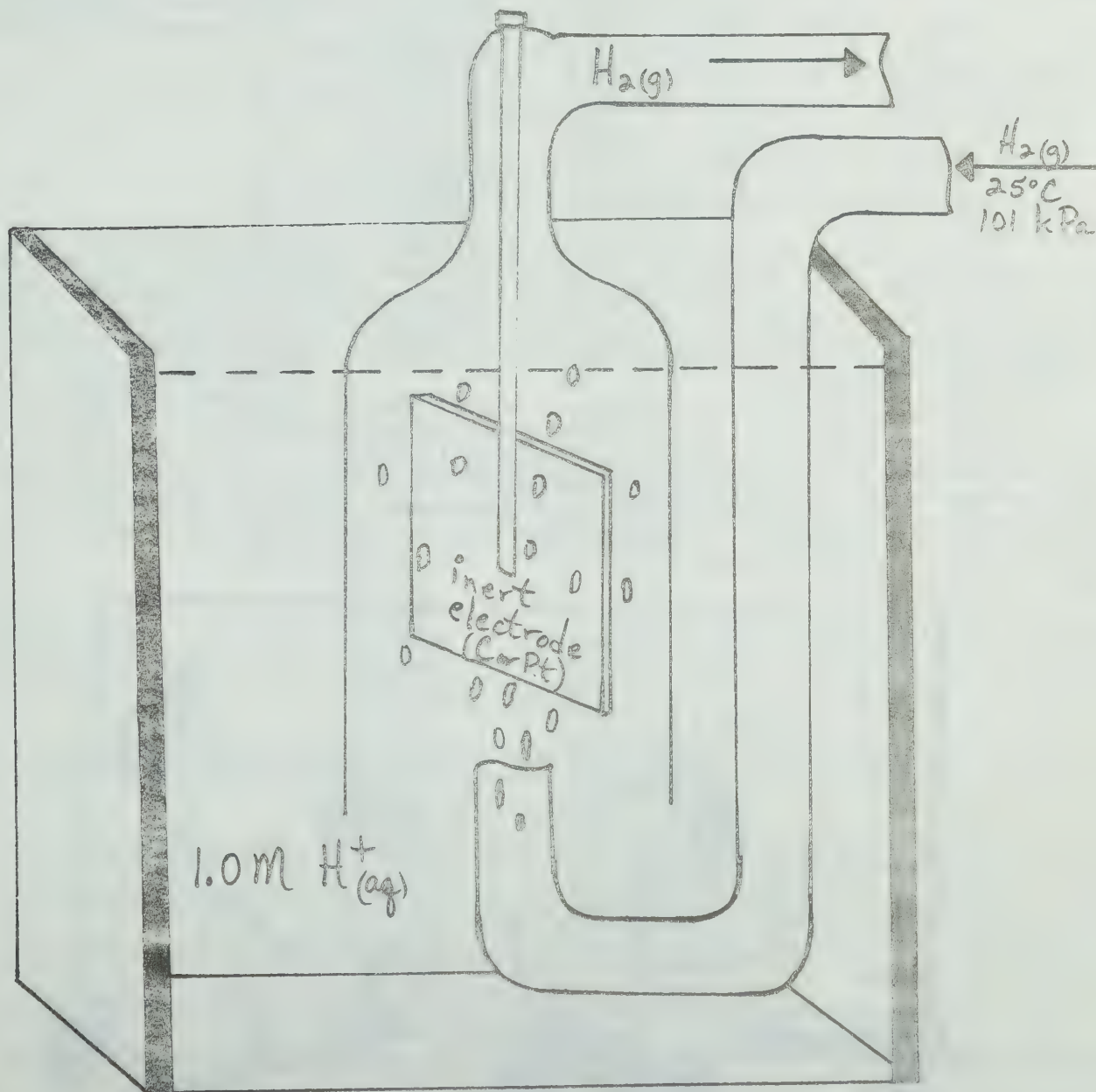
The  $\text{Zn}_{(\text{aq})}^{2+}$  ions go into the solution while the electrons remain on the zinc electrode. This half-reaction produces an excess of electrons on the zinc electrode and an excess of positively charged  $\text{Zn}_{(\text{aq})}^{2+}$  ions in the solution surrounding the zinc electrode. The electrode where oxidation occurs is called the anode. (L.E.O.A.)

Electrons move from the zinc electrode where they are in excess, through the connecting wire, to the copper electrode where there is a shortage of electrons. In general, electrons flow from the anode to the cathode of an electrochemical cell. In the solution positive ions (cations) migrate toward the copper electrode where there is an excess of negative ions around the electrode. The negative ions (anions) migrate toward the zinc electrode where there is an excess of positive ions around the electrode. In electrochemical cells anions move toward the anode and cations move toward the cathode. The migration of ions is essential to the operation of the cell since the accumulation of ionic charge in the solution around the electrodes would oppose the movement of electrons. The flow of electrons through the connecting wire and the flow of ions through the solution maintains the overall electrical neutrality of the electrochemical cell.

$E^\circ$  VALUES

In an electrochemical cell chemical energy is converted to electrical energy. For any electrochemical cell the energy possessed by the electrons can be measured by using a voltmeter. (The volt is discussed on page M54.)

The half reactions listed in the *ALCHEM* reduction potential table have voltage values assigned to them. These voltage values are called *reduction potentials* or  $E^\circ$  values. The reduction potentials were obtained by comparing each half reaction to a standard. Chemists have arbitrarily selected the hydrogen half-cell as a standard and have compared all other half-cells to the hydrogen half-cell. The comparisons were done at standard conditions (i.e.,  $25^\circ\text{C}$ , 101 kPa pressure, using 1.00 M solutions of the ions). A positive reduction potential implies that the substance has a greater tendency to attract electrons than does a hydrogen ion. A negative reduction potential implies that the substance has less tendency to attract electrons than a hydrogen ion. A hydrogen half-cell is pictured in Figure M3.



Hydrogen Half-Cell

Figure M3

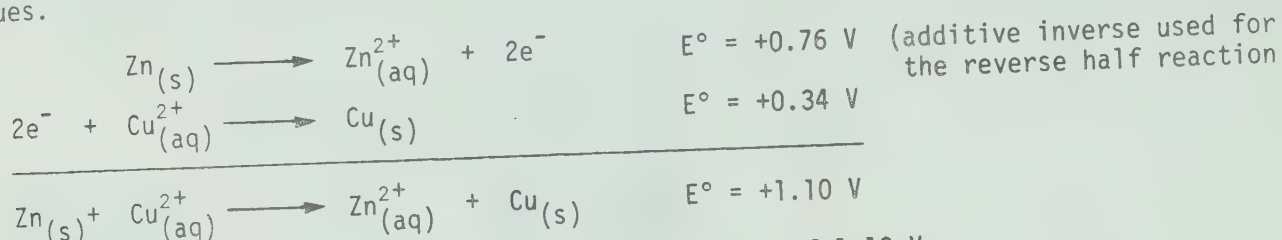
## ELECTROCHEMISTRY

## PREDICTING CELL VOLTAGES

The voltage of any electrochemical cell operating at standard conditions can be predicted from the  $E^\circ$  values listed in reduction potential tables. The  $E^\circ$  value for the reverse half-reaction is simply the negative (additive inverse) of the value listed. The additive inverse of a reduction potential is called an *oxidation potential*.

Example:

Predict the voltage of the electrochemical cell pictured in Figure M2. Obtain the  $E^\circ$  values for each half reaction then add the two half-reactions and their  $E^\circ$  values.



The cell pictured in Figure M2 would have a voltage of 1.10 V.

A positive  $E^\circ$  value for an electrochemical cell means that the reactions proceed as written in the equations. A negative  $E^\circ$  value for a cell means that the reactions are the reverse of the ones written.  $E^\circ$  values can be calculated for any redox reaction. Positive  $E^\circ$  values indicate spontaneous redox reactions while negative  $E^\circ$  values indicate reactions that are not spontaneous. Does this method of predicting spontaneity agree with the method of oxidizing agent strengths?

In electrochemical cells the electrodes must be made of good conducting material to allow the flow of electrons. In half-cells where the reacting species is a metal atom the electrode can be made from a rod or a strip of that metal. In half-cells where the reacting species is a liquid, a gas, or an aqueous ion the electrode can be made from a solid conductor which does not itself react. Two commonly used inert electrodes are platinum foil and carbon rod. A hydrogen half-cell is made by bubbling  $\text{H}_2$  gas over an inert electrode. (See Figure M3)





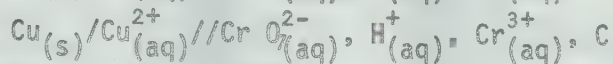
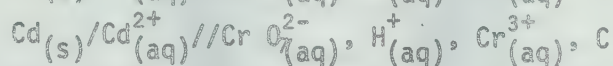
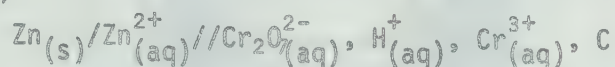
## ELECTROCHEMICAL CELLS - LAB M3

Purpose:

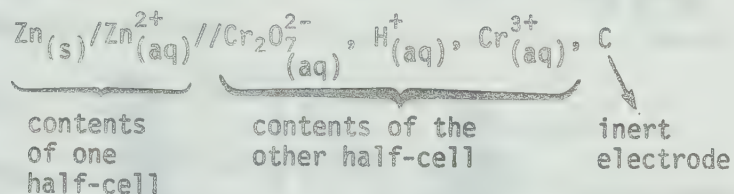
To analyze, construct, and measure the potential of various electrochemical cells.

Prelab Exercise:

A number of electrochemical cells will be constructed in the lab. Use the electrochemical cell diagrams on the next three pages to analyze the following cells which will be constructed in the lab. The 1.0 M solutions used are  $\text{ZnSO}_4(\text{aq})$ ,  $\text{CdSO}_4(\text{aq})$ ,  $\text{CuSO}_4(\text{aq})$  and acidic  $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ .

Example:

The shorthand notation used above is designed to convey the essential information about an electrochemical cell.



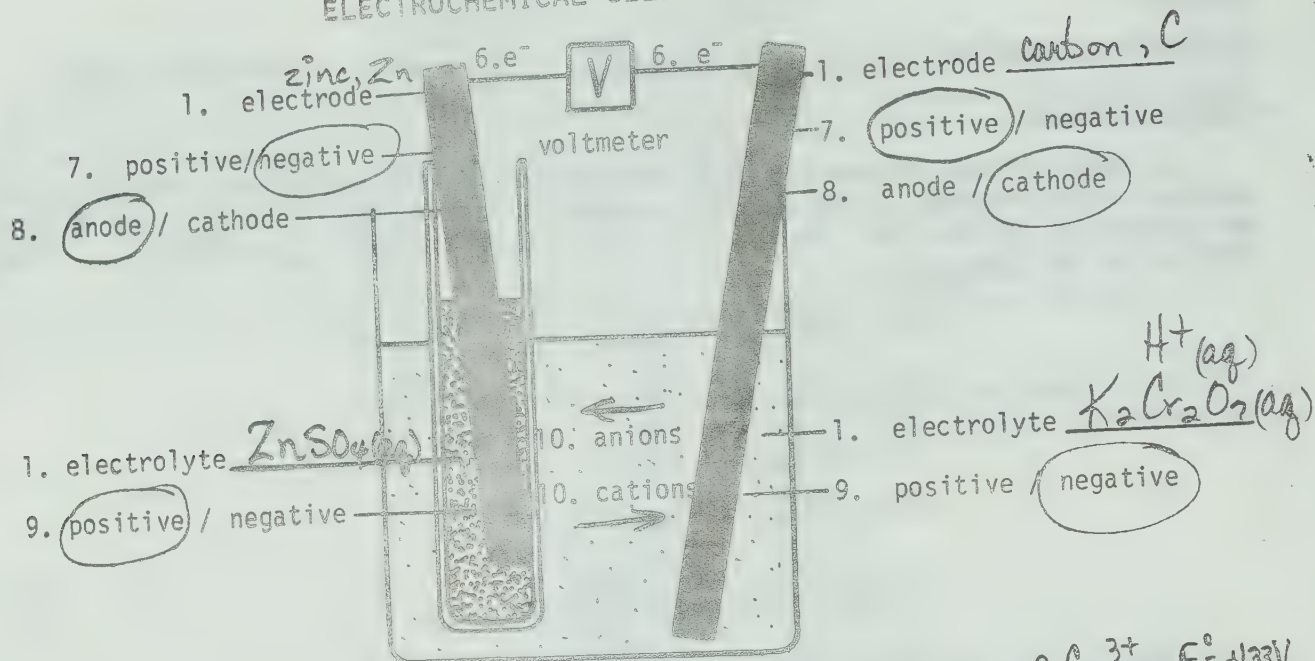
A vertical line (/) is used to separate the formulas for chemical species which are in different phases. A comma (,) is used to separate the formulas for chemical species which are in the same phase. A double line (//) is used to represent a salt bridge (e.g., a porous cup).

Use the following steps to analyze the cells to be constructed in Lab M3. The first is done as an example on the electrochemical cell analysis diagrams provided.

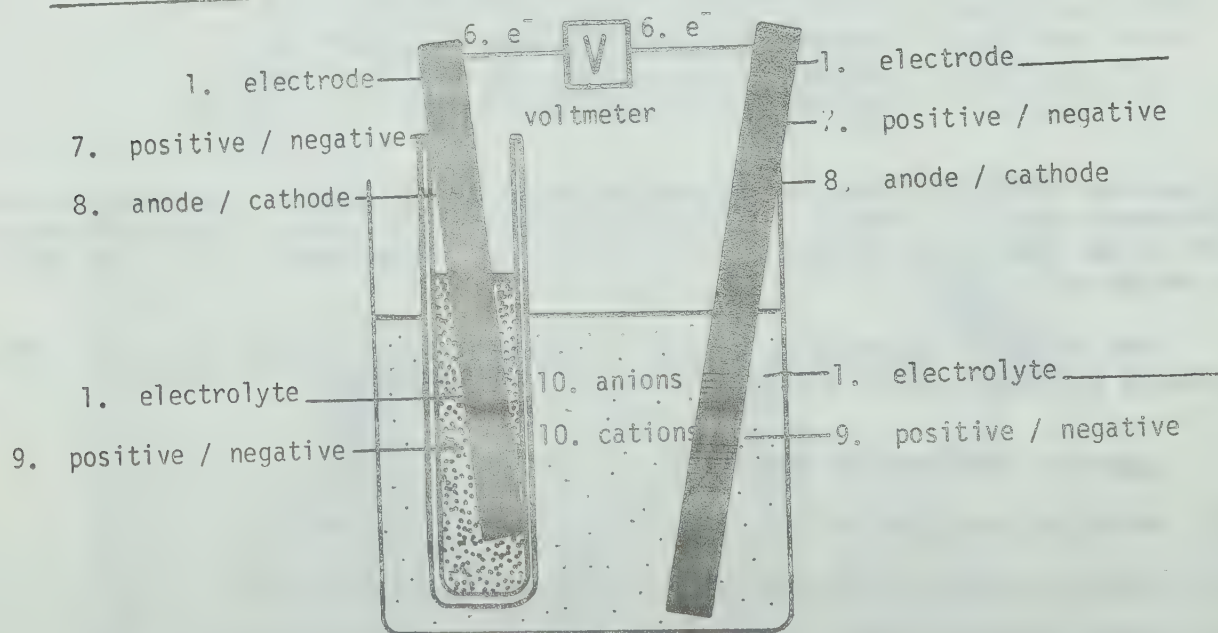
1. Label the electrode and electrolytes.
2. Write the reduction half reaction with its reduction potential.
3. Write the oxidation half reaction with its oxidation potential.
4. Write the balanced net reaction with its voltage value ( $E^\circ$  net).
5. Is the net reaction spontaneous as written in Step 4? Circle Yes/No on the diagram.

## ELECTROCHEMISTRY

## ELECTROCHEMICAL CELLS - LAB M3



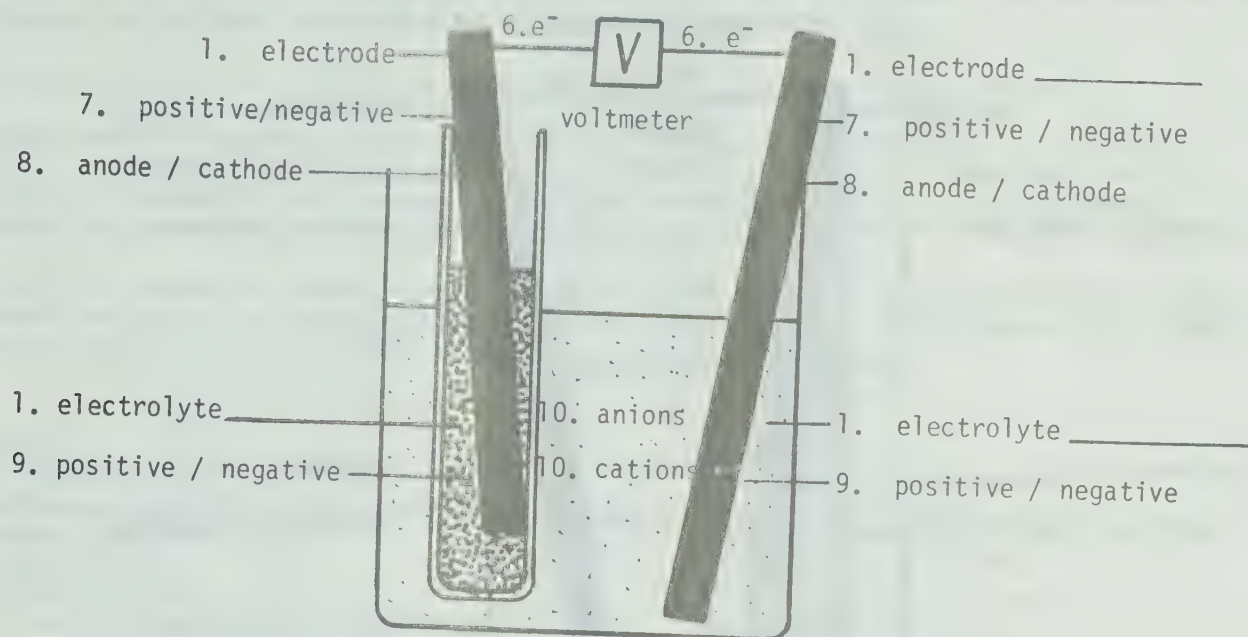
2. reduction half reaction:  $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 7\text{H}_2\text{O}(\text{l}) + 2\text{Cr}^{3+}(\text{aq})$   $E^\circ = +1.33\text{V}$
3. oxidation half reaction:  $3(\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-)$   $E^\circ = +0.76\text{V}$
4. net reaction:  $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 3\text{Zn}(\text{s}) \rightarrow 3\text{Zn}^{2+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l}) + 2\text{Cr}^{3+}(\text{aq})$   $E^\circ_{\text{net}} = +2.09\text{V}$
5. spontaneous: YES / NO



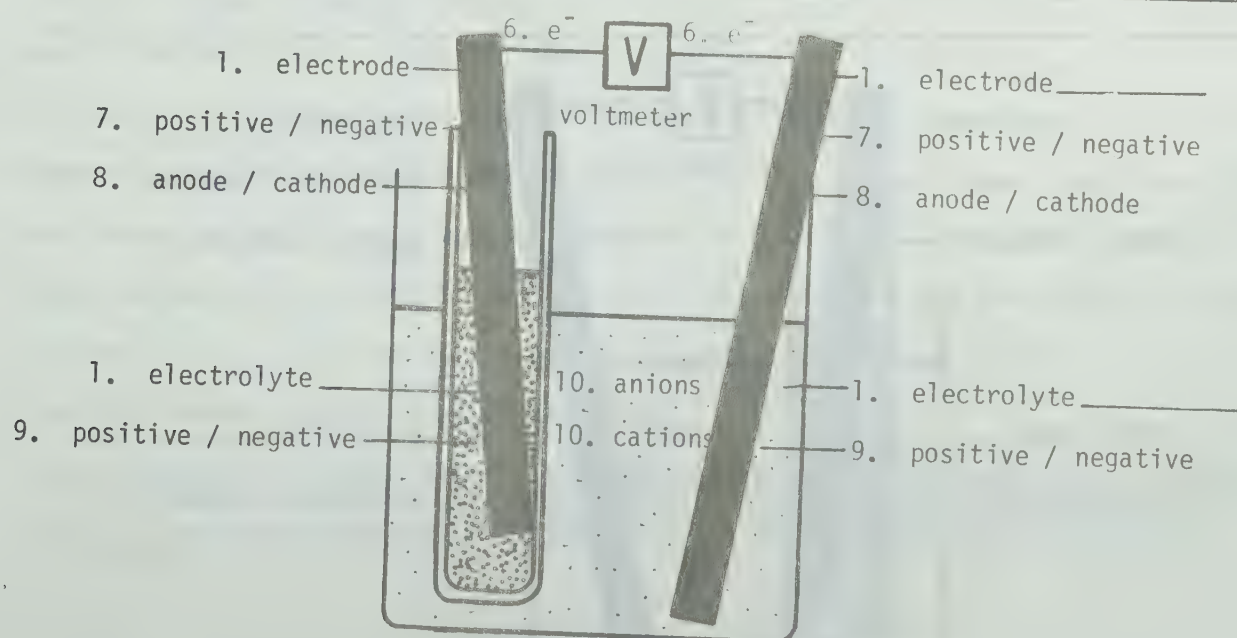
2. reduction half reaction:
3. oxidation half reaction:
4. net reaction:
5. spontaneous: YES / NO

## ELECTROCHEMISTRY

## ELECTROCHEMICAL CELLS - LAB M3



2. reduction half reaction: \_\_\_\_\_
3. oxidation half reaction: \_\_\_\_\_
4. net reaction: \_\_\_\_\_
5. spontaneous: YES / NO

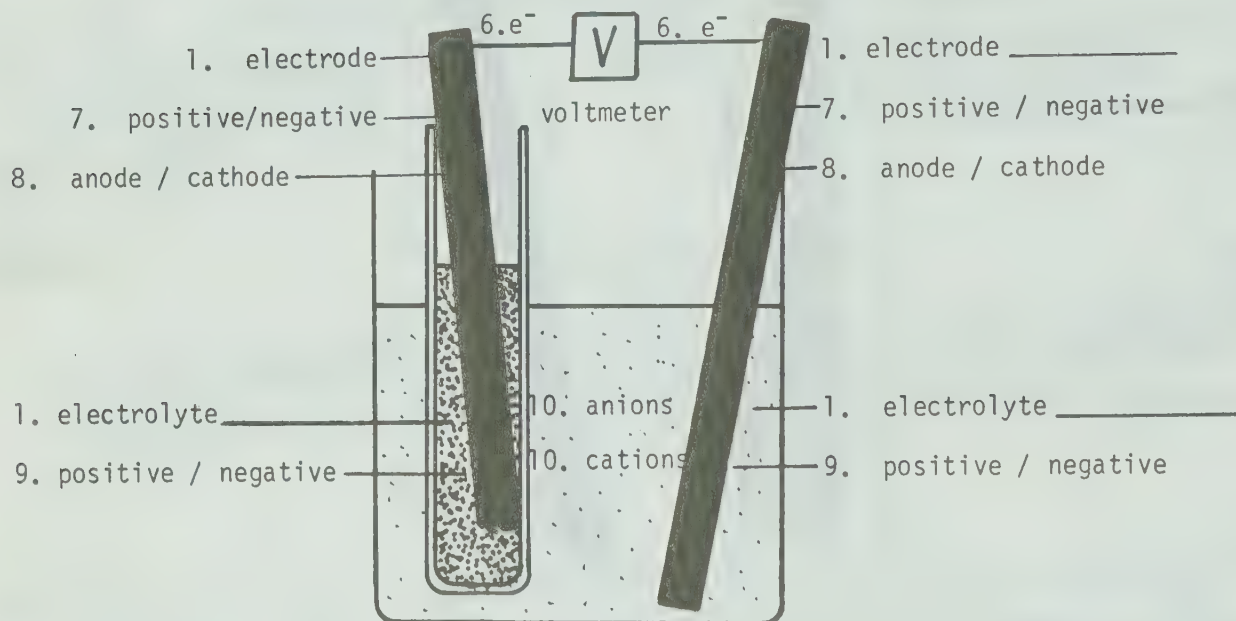


2. reduction half reaction: \_\_\_\_\_
3. oxidation half reaction: \_\_\_\_\_
4. net reaction: \_\_\_\_\_
5. spontaneous: YES / NO

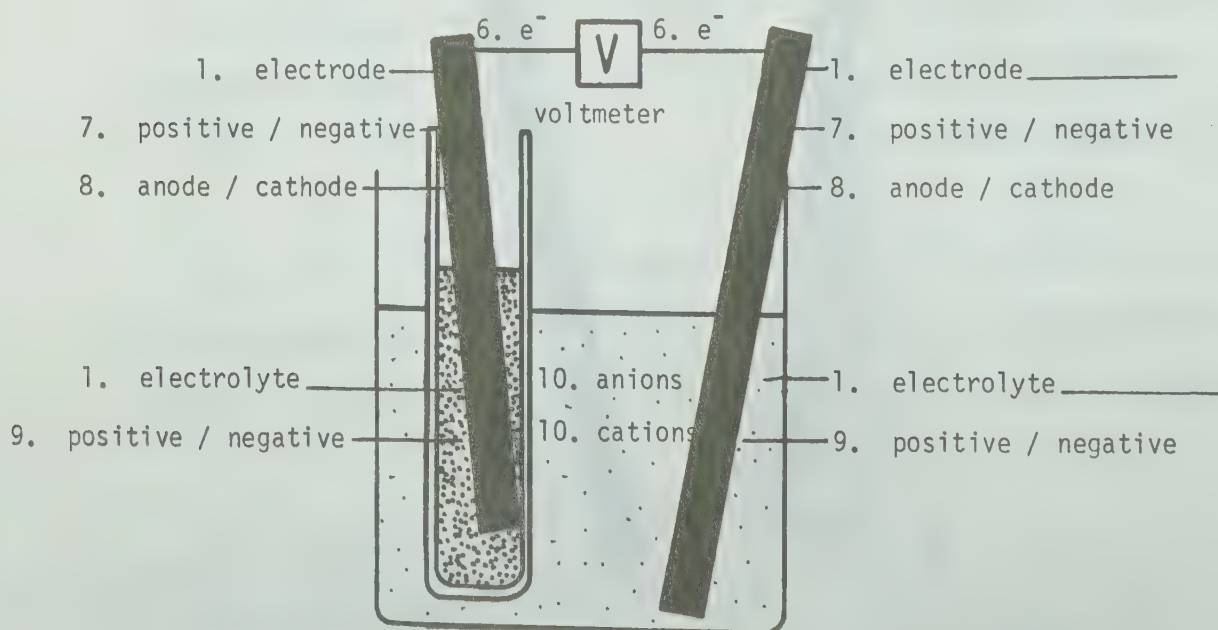


## ELECTROCHEMISTRY

## ELECTROCHEMICAL CELLS - LAB M3



2. reduction half reaction:
3. oxidation half reaction:
4. net reaction:
5. spontaneous: YES / NO



2. reduction half reaction:
3. oxidation half reaction:
4. net reaction:
5. spontaneous: YES / NO

## ELECTROCHEMICAL CELLS - LAB M3

6. From the half reactions determine the direction of electron flow. Use an arrow on the diagram to indicate the direction of electron flow.
7. From the direction of electron flow indicate the charge on each electrode.
8. From the half reactions label the anode and cathode. (Remember G.E.R.C. and L.E.O.A.)
9. From the change in ionic charge in the half reactions indicate the predominant ionic charge in the solution surrounding each electrode.
10. From the predominant ionic charge in the solution surrounding each electrode determine the direction of anion and cation migration. Use arrows on the diagram to indicate the direction of anion and cation migration.

Materials:

- |  |   |
|--|---|
| 1 - voltmeter (complete with connecting wires) | 1 - 10 ml graduated cylinder                                |
| 1 - porous cup                                 | 10 ml - 1.0 M $\text{H}_2\text{SO}_4(\text{aq})$            |
| 1 - 250 ml beaker                              | 100 ml - 1.0 M $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ |
| 4 - 150 ml beakers                             | 100 ml - 1.0 M $\text{CdSO}_4(\text{aq})$                   |
| 1 - 10 mm x 150 mm strip of cadmium            | 100 ml - 1.0 M $\text{CuSO}_4(\text{aq})$                   |
| 1 - 10 mm x 150 mm strip of copper             | 100 ml - 1.0 M $\text{ZnSO}_4(\text{aq})$                   |
| 1 - 10 mm x 150 mm strip of zinc               | steel wool  |
| 1 - carbon electrode                           |   |

Procedure:

1. Use labeled 150 ml beakers to obtain about 100 ml of 1.0 M aqueous solutions of  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{CdSO}_4$ ,  $\text{CuSO}_4$ , and  $\text{ZnSO}_4$ .
2. Use a 10 ml graduated cylinder to obtain about 10 ml of 1.0 M  $\text{H}_2\text{SO}_4(\text{aq})$ .
3. Add the 10 ml of  $\text{H}_2\text{SO}_4(\text{aq})$  to the labeled beaker containing  $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ .
4. Place a carbon electrode in a 250 ml beaker.
5. Pour the acidic  $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$  solution prepared in Step 3 into the 250 ml beaker.
6. Clean the surface of a zinc strip with steel wool and place the zinc strip in a porous cup.
7. Add the  $\text{ZnSO}_4(\text{aq})$  solution to the porous cup until it is about 2/3 full.
8. Place the porous cup into the 250 ml beaker.
9. Connect the positive (red) terminal of the voltmeter to the cathode of the electrochemical cell and connect the negative (black) terminal of the voltmeter to the anode of the cell. (Refer to the prelab exercise to determine which electrode is the anode and which is the cathode.)

## ELECTROCHEMISTRY

## ELECTROCHEMICAL CELLS - LAB M3

10. Record the voltmeter reading in the data table.
11. Look for signs of a chemical reaction around the anode and cathode. Record any observations in the data table.
12. Take the porous cup out of the 250 ml beaker, remove the zinc strip and pour the  $\text{ZnSO}_4(\text{aq})$  back into the labeled 150 ml beaker.
13. Rinse the porous cup with tap water.
14. Repeat Steps 6 - 13 using a cadmium strip in the  $\text{CdSO}_4$  solution.
15. Repeat Steps 6 - 13 using a copper strip in the  $\text{CuSO}_4$  solution.
16. Remove the carbon electrode from the 250 ml beaker and pour the  $\text{K}_2\text{Cr}_2\text{O}_7$  solution back into the labeled 150 ml beaker.
17. Rinse the 250 ml beaker with tap water.
18. Repeat Steps 4 - 13 using a  $\text{Zn}/\text{Zn}^{2+}$  half-cell in the porous cup and a  $\text{Cu}^{2+}_{(\text{aq})}/\text{Cu}_{(\text{s})}$  half-cell in the 250 ml beaker.
19. Repeat Steps 4 - 13 using a  $\text{Zn}/\text{Zn}^{2+}$  half-cell in the porous cup and a  $\text{Cd}^{2+}_{(\text{aq})}/\text{Cd}_{(\text{s})}$  half-cell in the 250 ml beaker.
20. Repeat Steps 4 - 13 using a  $\text{Cd}/\text{Cd}^{2+}$  half-cell in the porous cup and a  $\text{Cu}^{2+}_{(\text{aq})}/\text{Cu}_{(\text{s})}$  half-cell in the 250 ml beaker.
21. Dispose of the metal strips and aqueous solutions as directed by the teacher.

Observations:

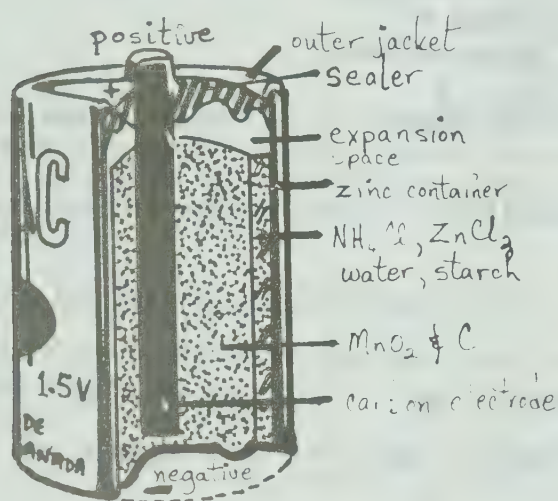
	Predicted Voltage	Observed Voltage	Visual Observations
$\text{Zn}_{(\text{s})}/\text{Zn}^{2+}_{(\text{aq})} // \text{Cr}_2\text{O}_7^{2-}_{(\text{aq})}, \text{H}^{+}_{(\text{aq})}, \text{Cr}^{3+}_{(\text{aq})}, \text{C}$			
$\text{Cd}_{(\text{s})}/\text{Cd}^{2+}_{(\text{aq})} // \text{Cr}_2\text{O}_7^{2-}_{(\text{aq})}, \text{H}^{+}_{(\text{aq})}, \text{Cr}^{3+}_{(\text{aq})}, \text{C}$			
$\text{Cu}_{(\text{s})}/\text{Cu}^{2+}_{(\text{aq})} // \text{Cr}_2\text{O}_7^{2-}_{(\text{aq})}, \text{H}^{+}_{(\text{aq})}, \text{Cr}^{3+}_{(\text{aq})}, \text{C}$			
$\text{Zn}_{(\text{s})}/\text{Zn}^{2+}_{(\text{aq})} // \text{Cu}^{2+}_{(\text{aq})}/\text{Cu}_{(\text{s})}$			
$\text{Zn}_{(\text{s})}/\text{Zn}^{2+}_{(\text{aq})} // \text{Cd}^{2+}_{(\text{aq})}/\text{Cd}_{(\text{s})}$			
$\text{Cd}_{(\text{s})}/\text{Cd}^{2+}_{(\text{aq})} // \text{Cu}^{2+}_{(\text{aq})}/\text{Cu}_{(\text{s})}$			



## COMMERCIAL CELLS

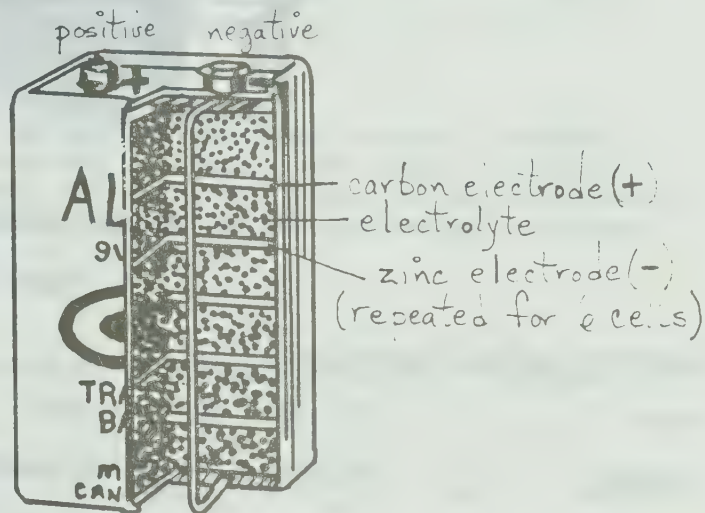
Several types of electrochemical cells and batteries are available commercially. Batteries are made by connecting two or more cells in series so that the voltage of the battery is the sum of the voltages of the individual cells. Some commercial cells cannot be effectively recharged so when the chemicals in the cell eventually become exhausted the cell must be replaced. Other commercial cells can be recharged by reversing the current through the cell by means of a battery charger.

Dry Cell (Leclanché Cell),  $E^\circ = 1.55 \text{ V}$



Dry (Leclanché) Cell

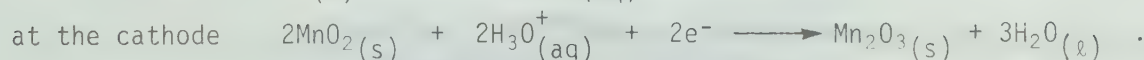
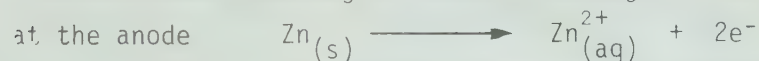
Figure M4



9 Volt Transistor Battery

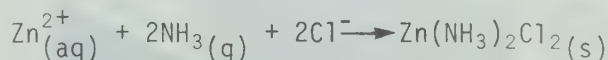
Figure M5

The reactions occurring in the cell during discharge are:

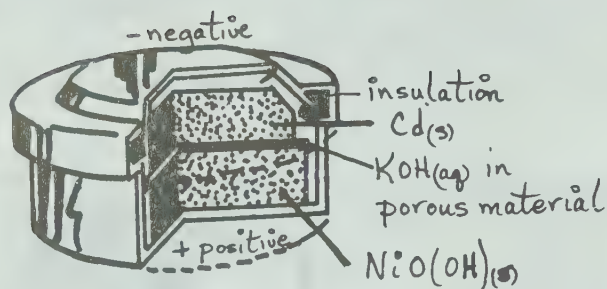


The consumption of  $\text{H}_3\text{O}^{+}$  during the operation of the cell produces  $\text{OH}^{-}$  ions (See ALCHEM Unit N - Acids and Bases).

The  $\text{OH}^{-}$  ions cause the following irreversible side reactions to occur.

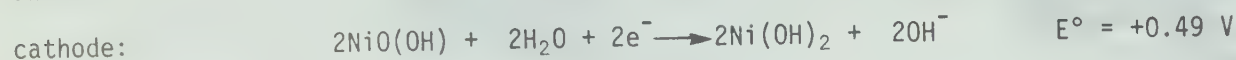
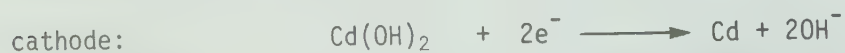
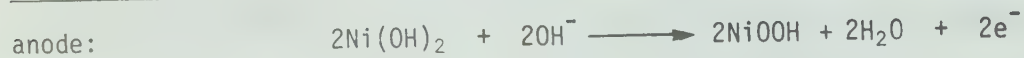


Because of the above reactions, the cell is only partially rechargeable. Dry cells are rechargeable to such a small extent that it is rarely done in practice.

Nickel-Cadmium Cell

A Nickel-Cadmium Cell

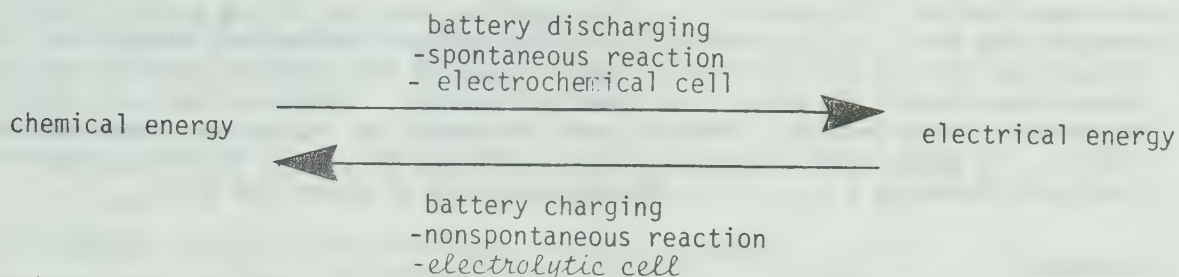
Figure M6

Reactions During Discharging:Reactions During Charging:Question:

How many nickel-cadmium cells would be needed to make a 10 V battery?

Reversing Redox Reactions:

Chemical energy is changed into electrical energy in an *electrochemical cell*. Electrical energy is changed into chemical energy in an *electrolytic cell*. Charging a battery illustrates the operation of an *electrolytic cell*.

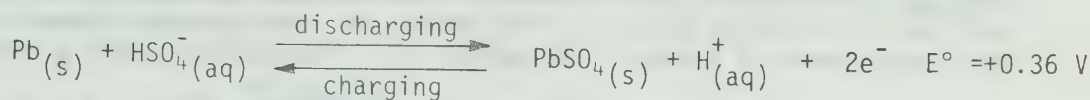


A battery may be charged if the products of the battery half reactions are still present and/or have the mobility to move toward the appropriate electrode. Some gases and solids produced may not be able to fill these requirements and so not all batteries are rechargeable. A minimum charging voltage (equal to the discharging voltage) must be applied to the battery terminals.

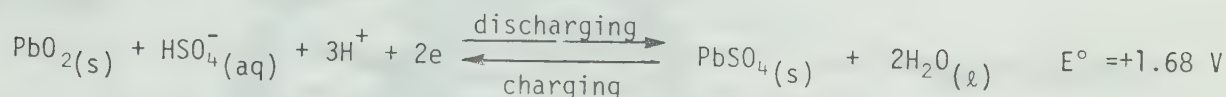
Charging a Car Battery (Lead Storage Battery)

Recall the equation for the anode and cathode half reactions and the net equation presented earlier.

Anode:



Cathode:



Net reaction:

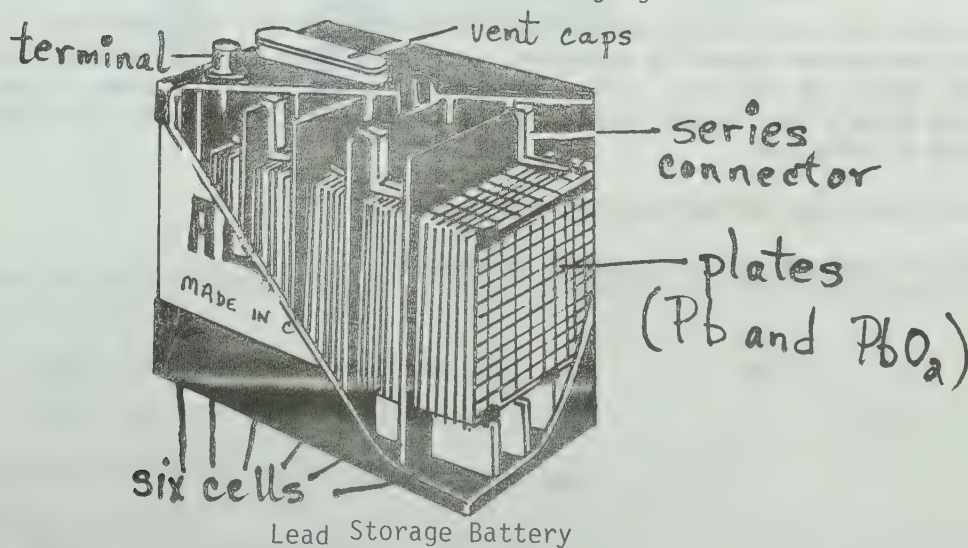
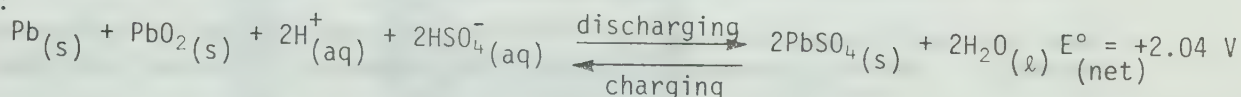
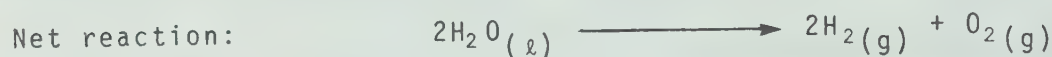
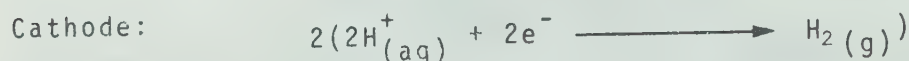


Figure M7

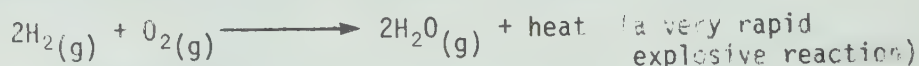


Boosting

When charging or boosting a car battery the negative (black) terminal of the battery charger or booster battery is connected to the negative terminal of the battery being charged or boosted, and then positive terminals are connected. The battery charger will force electrons through the battery in a reverse direction causing the chemical reaction to reverse (converting electrical energy into chemical energy). Boosting does not usually charge the battery being boosted. Boosting has the effect of replacing a poor battery with a better battery. An undesirable reaction which occurs (particularly in older batteries) when charging or boosting a battery is the electrolysis of water (in  $\text{H}_2\text{SO}_4(\text{aq})$ ).



Besides the annoyance of having to replace the water, a dangerous situation can arise due to the production of hydrogen gas. A rapid evolution of hydrogen gas may occur when boosting a particularly poor battery. The hydrogen gas may explode when ignited by a spark; such sparks are often produced when making the final battery connection. Besides the danger of flying pieces of battery, the danger of flying sulfuric acid exists.

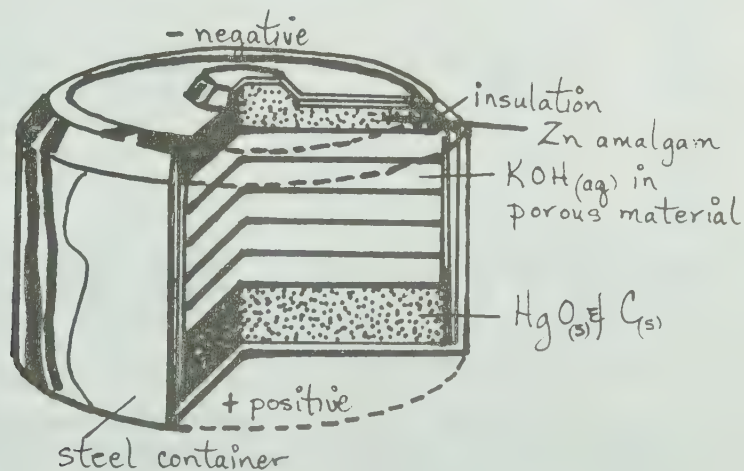
Boosting Safety

If one car battery is being used to boost another take the following precautions:

1. Make the last connection (and the first disconnection) at the car with the good battery. (The last connection and the first disconnection usually produce a spark.)
2. Make the last connection as far away from the battery as possible. If the last connection is to the ground (usually negative) terminal, then the connection can be made to any metal object on the car. Since the ground cable on the battery is connected directly to the motor, the booster cable can be connected to the motor and the same boosting action is obtained.
3. Do not lean over either battery when boosting.
4. Wear eye protection (i.e. goggles or glasses).

## AN OVERVIEW OF COMMERCIAL CELLS

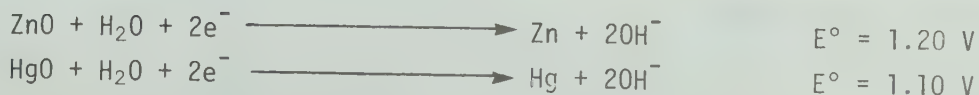
1. Write the overall equation for the discharging of a dry cell with its  $E^\circ$  net value. (Omit the side reactions.)
2. Why is it not practical to recharge a dry cell?
3. Write the formulas of five compounds found in a *dead* dry cell.
4. Write the overall equation for the discharging of a nickel-cadmium cell with its  $E^\circ$  (net) value. How many *ni-cad* cells are needed to make a 10 V battery?
5. A mercury cell (used in pacemakers for persons with heart conditions) is diagrammed in Figure M8



A Mercury Cell

Figure M8

The changes which occur during the operation of a mercury cell can be represented by the equations:



Use the above equations to answer the following questions:

anode reaction during operation: \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

cathode reaction during operation: \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

overall reaction during operation: \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

## COMMERCIAL CELLS

6. Write the equation for the oxidation half reaction for the corroding of copper connection wires on a battery.
7. What is the  $E^\circ$  value for the net reaction involving the electrolysis of water in a lead storage battery?
8. In very cold weather the voltage of a battery drops negligibly and yet the efficiency of the battery drops drastically. Explain.
9. The reduction half reactions and potentials for a silver-cadmium cell are given below. Write down and label the anode and cathode half reactions, the net equation, and determine the  $E^\circ$  net for the cell.



10. *Fuel cells* are electrochemical cells which employ chemicals commonly used as fuels. Methane and hydrogen, for example, are common fuels which may be employed in fuel cells. Converting these fuels directly into electrical energy is much more efficient than burning them in a steam electrical generating plant. The efficiency of the fuel cell is about 70%, while the efficiency of the power plant is about 20-30%.

The reduction half reactions and potentials for a methane-oxygen fuel cell are given below. Write down and label the anode and cathode half reactions, the net equation, and determine the  $E^\circ$  net for the cell.



See diagram on page M68.



## ELECTROLYSIS

In electrochemical cells, chemical energy produces electrical energy from spontaneous chemical reactions. The reverse of this system is the process of *electrolysis*. In an *electrolytic cell* electrical energy is used to force a nonspontaneous chemical change to occur. Electrochemical cells may be viewed as exothermic chemical reactions which release electrical energy. Electrolytic cells may be viewed as endothermic chemical reactions, which must absorb electrical energy in order to occur.

Positive  $E^\circ_{\text{net}}$  values for electrochemical cells indicate the tendency for the chemical reaction to occur spontaneously. Electrolytic cells have negative  $E^\circ_{\text{net}}$  values which indicate the *minimum* voltage that must be applied to the cell to *cause* the chemical reaction to occur.

Many useful reactions center around the use of electricity to produce chemical changes. Examples include electroplating of metals and electrolysis of water to produce hydrogen and oxygen.

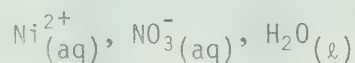
The method used for predicting redox reactions in a beaker can be modified to predict the most likely reactions to occur in an electrolytic cell.

Example:

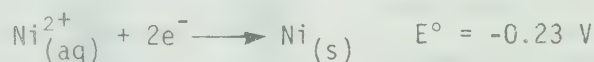
An electric current is passed through an aqueous solution of nickel(II) nitrate. Predict the anode and cathode reactions, write a balanced equation for the overall reaction, and determine the minimum voltage required to produce the reactions.

Step 1:

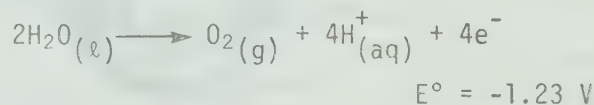
List all the chemical species present in the solution.

Step 2:

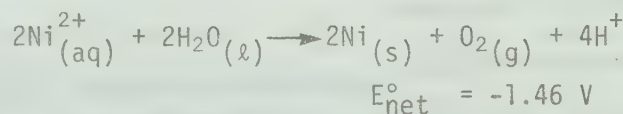
Use the reduction potential table to identify the strongest oxidizing agent and write its half reaction and  $E^\circ$  value. This is the *cathode* reaction.

Step 3:

Use the reduction potential table to identify the strongest reducing agent and write its half reaction and  $E^\circ$  value. This is the *anode* reaction.

Step 4:

Write the balanced net ionic equation for the overall reaction and determine  $E^\circ_{\text{net}}$ .

Step 5:

Determine the minimum voltage required to produce the reactions. The minimum voltage required is equal to the additive inverse of the  $E^\circ_{\text{net}}$  value for the overall reaction.

$$\text{minimum voltage} = +1.46 \text{ V}$$

## QUALITATIVE ASPECTS OF ELECTROLYSIS - DEMO M1

Purpose:

1. To predict the products of several electrolytic cells.
2. To observe several electrolytic cells in operation.
3. To determine experimentally the products of several electrolytic cells.

Prelab Exercise:

Predict the anode and cathode reactions for the electrolysis of each of the following substances. Write the net ionic equation for the overall reaction and determine the minimum voltage required to produce the reaction.

Electrolysis of Aqueous Sodium Sulfate

anode reaction: \_\_\_\_\_

cathode reaction: \_\_\_\_\_

overall reaction: \_\_\_\_\_

minimum voltage: \_\_\_\_\_

Electrolysis of Hydrochloric Acid

anode reaction: \_\_\_\_\_

cathode reaction: \_\_\_\_\_

overall reaction: \_\_\_\_\_

minimum voltage: \_\_\_\_\_

Electrolysis of Aqueous Potassium Iodide

anode reaction: \_\_\_\_\_

cathode reaction: \_\_\_\_\_

overall reaction: \_\_\_\_\_

minimum voltage: \_\_\_\_\_

Electrolysis of Aqueous Copper(II) Sulfate

anode reaction: \_\_\_\_\_

cathode reaction: \_\_\_\_\_

overall reaction: \_\_\_\_\_

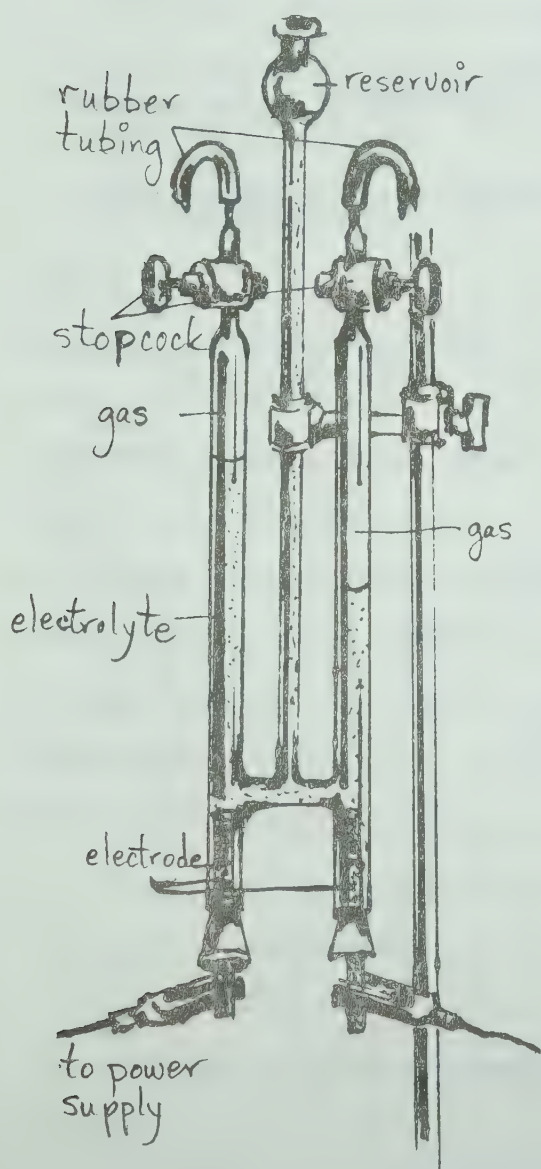
minimum voltage: \_\_\_\_\_

## QUALITATIVE ASPECTS OF ELECTROLYSIS - DEMO M1

Materials:

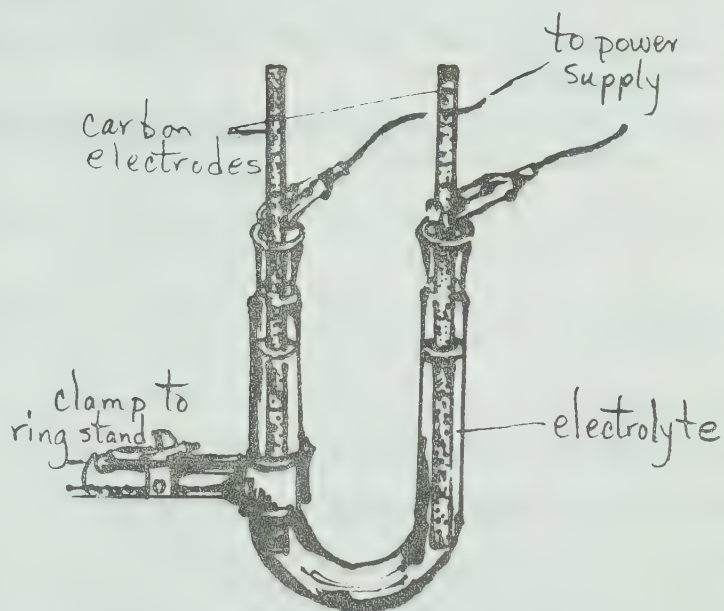
- 1 - low voltage D.C. power supply
- 2 - Hoffman's Apparatus (set up)
- 2 - U-tubes
- 4 - carbon electrodes
- 2 - utility clamps
- 1 - 10 ml measuring pipet
- 1 - dropping bottle of 1.0 M NaI
- 1 - dropping bottle of  $\text{CCl}_4$
- 4 - test tubes (13 x 100 mm)
- 4 - 50 ml beakers
- 1 - ring stand

- 300 ml 1.0 M  $\text{Na}_2\text{SO}_4(\text{aq})$
- 300 ml 1.0 M  $\text{HCl}(\text{aq})$
- 200 ml 1.0 M  $\text{KI}(\text{aq})$
- 200 ml 1.0 M  $\text{CuSO}_4(\text{aq})$
- red litmus paper
- blue litmus paper
- wood splints
- matches



Hoffman's Apparatus

Figure M9



U-tube Electrolysis Apparatus

Figure M10



## QUALITATIVE ASPECTS OF ELECTROLYSIS - DEMO M1

Procedure:Electrolysis of Aqueous Sodium Sulfate (Hoffman's Apparatus)

1. The apparatus will be set up. If the solution level is down add more solution to the reservoir.
2. Connect the power supply and observe the reaction.
3. Allow the reaction to proceed for 5 - 10 minutes. Record any observations.
4. Disconnect the power supply.
5. Read and record the volumes of each gas produced.
6. Fill a test tube with the gas from around the anode and test it with a *glowing* splint. Record the observation.
7. Fill a test tube with the gas from around the cathode and test it with a *burning* splint. Record the observation.
8. Remove some of the solution from around the anode and test it with litmus paper. Record the observation.
9. Remove some of the solution from around the cathode and test it with litmus paper. Record the observation.

Observations:Electrolysis of Aqueous Sodium Sulfate

changes during electrolysis \_\_\_\_\_

volumes of gases produced:                      anode \_\_\_\_\_ cathode \_\_\_\_\_

identification of the anode gas \_\_\_\_\_

identification of the cathode gas \_\_\_\_\_

litmus paper in anode solution \_\_\_\_\_

litmus paper in cathode colution \_\_\_\_\_

anode half reaction \_\_\_\_\_

cathode half reaction \_\_\_\_\_

overall reaction \_\_\_\_\_

## QUALITATIVE ASPECTS OF ELECTROLYSIS - DEMO M1

Procedure:Electrolysis of Hydrochloric Acid (Hoffman's Apparatus)

1. The apparatus will be set up. If the acid level is low add more solution to the reservoir.
2. Connect the power supply and observe the reaction. Record any observations.
3. Allow the reaction to proceed for 5 - 10 minutes.
4. Disconnect the power supply.
5. Note the color and odor of the gas produced at the anode. *Caution!*
6. Test the gas produced at the cathode with a burning splint. Record the observation.
7. Remove about 2 ml of the solution from around the anode, place in a test tube and add an equal volume of 1.0 M NaI. Add  $\text{CCl}_4$  to the solution and shake the solution. Record the observation.
8. Remove about 2 ml of the solution from around the cathode and test it with litmus paper. Record the observation.

Observations:Electrolysis of Hydrochloric Acid

changes during electrolysis \_\_\_\_\_

identification of anode gas: color \_\_\_\_\_ odor \_\_\_\_\_

identification of cathode gas \_\_\_\_\_

NaI in anode solution: color of solution \_\_\_\_\_ color of  $\text{CCl}_4$  layer \_\_\_\_\_

litmus paper in cathode solution \_\_\_\_\_

anode half reaction \_\_\_\_\_

cathode half reaction \_\_\_\_\_

overall reaction \_\_\_\_\_

## ELECTROCHEMISTRY

## QUALITATIVE ASPECTS OF ELECTROLYSIS - DEMO M1

Procedure:Electrolysis of Aqueous Potassium Iodide (U-tube)

1. The U-tube assembly should be attached by a utility clamp to a ring stand.
2. Fill the U-tube with potassium iodide solution. Place a carbon electrode in each end of the U-tube.
3. Complete the circuit and allow the electrolysis to proceed.
4. Record changes which occur at the electrodes.
5. Allow electrolysis to proceed for 5 - 10 minutes.
6. Use a pipet to remove about 2 ml of solution from around the anode. Place the solution in a test tube and test it with 1 ml of  $\text{CCl}_4$ . Record the observation.
7. Use a pipet to remove about 2 ml of solution from the cathode side of the U-tube. Test the solution with litmus paper.

Observations:Electrolysis of Aqueous Potassium Iodide

changes during electrolysis \_\_\_\_\_

anode liquid plus  $\text{CCl}_4$  (color) \_\_\_\_\_

cathode liquid plus litmus \_\_\_\_\_

anode half reaction \_\_\_\_\_

cathode half reaction \_\_\_\_\_

overall reaction \_\_\_\_\_

Procedure:Electrolysis of Aqueous Copper(II) Sulfate (U-tube)

1. The U-tube assembly should be attached by a utility clamp to a ring stand.
2. Fill the U-tube with copper(II) sulfate solution. Place a carbon electrode in each end of the U-tube.
3. Complete the circuit and allow the electrolysis to proceed.
4. Record changes which occur at the electrodes.
5. Allow electrolysis to proceed for 5 - 10 minutes.
6. Use a pipet to remove about 2 ml of solution from around the anode. Test the solution with litmus paper. Record your observation.
7. Remove the carbon electrodes and describe any changes which occurred during electrolysis.



## QUALITATIVE ASPECTS OF ELECTROLYSIS - DEMO M1

Observations:Electrolysis of Aqueous Copper(II) Sulfate

changes during electrolysis \_\_\_\_\_

anode solution plus litmus \_\_\_\_\_

condition of electrodes: anode \_\_\_\_\_

cathode \_\_\_\_\_

anode half reaction \_\_\_\_\_

cathode half reaction \_\_\_\_\_

overall reaction \_\_\_\_\_

Questions:

1. Complete the following summary.

Electrolyte	Cathode Product	Anode Product
$\text{Na}_2\text{SO}_4(\text{aq})$		
$\text{HCl}(\text{aq})$		
$\text{KI}(\text{aq})$		
$\text{CuSO}_4(\text{aq})$		

2. How do the actual products of electrolysis compare with the predictions made in the prelab exercise?

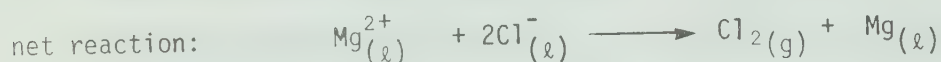
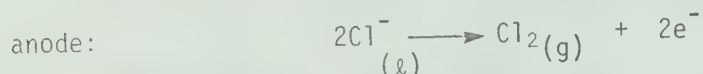
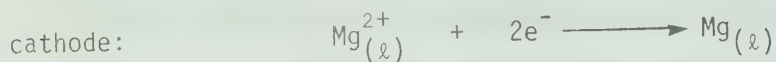
3. Half reactions which produce
- $\text{O}_2(\text{g})$
- tend to be quite slow. Is there any evidence of this tendency in this experiment?

## ELECTROCHEMISTRY

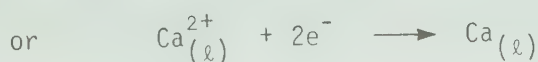
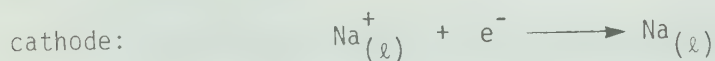
## ELECTROLYSIS

Electrolysis of Molten Magnesium Chloride

Another example of electrolysis is the production of magnesium from molten magnesium chloride. The reactions are:



The above reactions are involved in the industrial production of magnesium. The magnesium chloride is mixed with molten calcium chloride and sodium chloride. Therefore two other reactions are possible at the cathode.



The reduction of  $\text{Mg}^{2+}$  take precedence over the sodium and calcium reactions because it requires less voltage and has a relatively fast reaction rate. (The  $E^{\circ}$  values for molten ion half reactions can not be taken from the reduction potential table of aqueous ions.)

Note:

The prediction of products for the electrolysis of molten binary salts is usually fairly straight forward; i.e., the element of the cation is formed at the cathode and the element of the anion is formed at the anode.

An industrial application of the electrolysis of molten binary salts will be covered at the end of this unit (i.e., the Downs Cell).

## ELECTROCHEMISTRY

## QUALITATIVE ASPECTS OF ELECTROLYSIS

For each of the following electrolysis reactions

- a. Write equations for the half reactions and the net cell reaction.
  - b. Calculate the minimum voltage that would be required to cause the electrolysis to occur.
1. An aqueous solution of nickel(II) chloride is electrolyzed.
  2. An aqueous solution of potassium sulfate is electrolyzed.
  3. An aqueous solution of lead(II) nitrate is electrolyzed.
  4. Molten sodium iodide is electrolyzed. (Omit the  $E^\circ$ 's and the net minimum voltage. Why?)
  5. A solution of aqueous sodium bromide and aqueous zinc chloride are mixed in an electrolytic cell using inert electrodes. The products are bromine gas and zinc metal.



## ELECTRICAL UNITS

The quantitative study of electricity requires an understanding of electrical charge, current, and potential difference. (The study of potential difference is delayed until required later.)

Charge (Q)

The unit of electrical charge is the coulomb (C). One electron has a charge of  $1.60 \times 10^{-19}$  C. One mole of electrons has a charge of  $9.65 \times 10^4$  C. The # moles of electrons involved in a half reaction can be calculated from the following equation.

$$\# \text{ moles } e^- = \frac{Q}{9.65 \times 10^4}$$

$\xrightarrow{\text{charge in coulombs (C)}}$   
 $\xrightarrow{\# \text{ coulombs per mole } e^- \text{ (C/mol)}}$

Current (I)

Electric current is defined as the rate of flow of charge. It is measured in amperes (A). 1 ampere = 1 coulomb/second (or 1A = 1C/s). In symbols,

$$\text{current in amperes } I = \frac{\text{charge in coulombs}}{\text{time in seconds}}$$

In electrochemistry this equation is often used in the form,  $Q = It$ .

Since  $Q = It$ ,

$$\# \text{ moles } e^- = \frac{It}{9.65 \times 10^4}$$

Example:

Determine the number of moles of electrons supplied by a dry cell supplying a current of 0.100 A for 5 0.0 min to a transistor radio.

$$\begin{aligned} \# \text{ moles } e^- &= \frac{It}{9.65 \times 10^4} \\ &= \frac{0.100 \text{ A} \times 5.0 \text{ min} \times 60.0 \text{ s/min}}{9.65 \times 10^4 \text{ C/mol}} \\ &= 0.00311 \text{ mol} \end{aligned}$$

## ELECTROCHEMISTRY

## QUANTITATIVE ASPECTS OF ELECTROLYSIS

The following examples illustrate the steps to be followed in solving electrolysis problems. Note that the same basic four steps are involved as for gravimetric and solution stoichiometry problems. A useful relationship in these problems is:

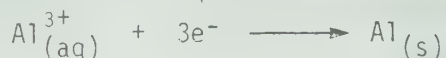
$$\# \text{ moles } e^- = \frac{Q}{9.65 \times 10^4} = \frac{It}{9.65 \times 10^4}$$

Example 1:

If 20.0 A of current flows through an electrolytic cell for 1.00 h, what mass of aluminum will be deposited at the cathode?

Step 1:

Write the balanced half reaction equation.

Step 2:

Determine the number of moles of electrons involved.

$$\begin{aligned} \# \text{ moles } e^- &= \frac{It}{9.65 \times 10^4} \\ &= \frac{20.0 \text{ C/s} \times 1.00 \text{ h} \times 60.0 \text{ min/h} \times 60.0 \text{ s/min}}{9.65 \times 10^4 \text{ C/mol}} \\ &= 0.746 \text{ mol} \end{aligned}$$

Step 3:

Determine the number of moles of element produced or reacted.

$$\begin{aligned} \# \text{ moles Al} &= \# \text{ moles } e^- \times \frac{\text{coefficient of Al}}{\text{coefficient of } e^-} \\ &= 0.746 \text{ mol} \times \frac{1}{3} \\ &= 0.249 \text{ mol} \end{aligned}$$

Step 4:

Determine the mass of the element produced or reacted.

$$\begin{aligned} \text{mass Al} &= \# \text{ moles} \times \text{molar mass} \\ &= 0.249 \text{ mol} \times 27.0 \frac{\text{g}}{\text{mol}} \\ &= 6.72 \text{ g} \end{aligned}$$

6.72 g of Al are produced

## ELECTROCHEMISTRY

## QUANTITATIVE ASPECTS OF ELECTROLYSIS

Example 2:

A student wishes to plate 5.87 g of Ni onto a hub cap from a 2.00 M solution of NiCl<sub>2</sub>. How long must the student run a 0.500 A current in order to produce the mass of Ni?

Step 1:

Write the balanced half reaction equation.

Step 2:

Determine the number of moles of element desired.

$$\begin{aligned} \# \text{ moles Ni} &= \text{mass/molar mass} \\ &= \frac{5.87 \text{ g}}{58.7 \text{ g/mol}} \\ &= 0.100 \text{ mol} \end{aligned}$$

Step 3:

Determine the number of moles of electrons required.

$$\begin{aligned} \# \text{ moles e}^{-} &= \# \text{ moles Ni} \times \frac{\text{coefficient of e}^{-}}{\text{coefficient of Ni}} \\ &= 0.100 \text{ mol} \times \frac{2}{1} \\ &= 0.200 \text{ mol} \end{aligned}$$

Step 4:

Determine the length of time the current must run.

$$\begin{aligned} \# \text{ moles e}^{-} &= \frac{It}{9.65 \times 10^4} \\ t &= \frac{\# \text{ moles e}^{-} \times 9.65 \times 10^4}{I} \\ &= \frac{0.200 \text{ mol} \times 9.65 \times 10^4 \text{ C/mol}}{0.500 \text{ C/s}} \\ &= 3.86 \times 10^4 \text{ s} \end{aligned}$$

The current must run for  $3.86 \times 10^4 \text{ s}$  or 10.7 h



## QUANTITATIVE ASPECTS OF ELECTROLYSIS

Example 3:

A certain electrolytic cell produced 21.3 g of chlorine gas from molten sodium chloride. This mass of chlorine was produced in 80 minutes. What was the average current during this time?

Step 1:

Write the balanced half reaction equation.

Step 2:

Determine the number of moles of element produced.

$$\begin{aligned} \# \text{ moles } \text{Cl}_2 &= \frac{\text{mass}}{\text{molar mass}} \\ &= \frac{21.3 \text{ g}}{70.9 \text{ g/mol}} \\ &= 0.300 \text{ mol} \end{aligned}$$

Step 3:

Determine the number of moles of electrons required.

$$\begin{aligned} \# \text{ moles } \text{e}^- &= \# \text{ moles } \text{Cl}_2 \times \frac{\text{coefficient of e}^-}{\text{coefficient of Cl}} \\ &= 0.300 \text{ mol} \times \frac{2}{1} \\ &= 0.600 \text{ mol} \end{aligned}$$

Step 4:

Determine the average current.

$$\begin{aligned} \# \text{ moles } \text{e}^- &= \frac{It}{9.65 \times 10^4} \\ I &= \frac{\# \text{ moles e}^- \times 9.65 \times 10^4}{t} \\ &= \frac{0.600 \text{ mol} \times 9.65 \times 10^4 \text{ C/mol}}{80 \text{ min} \times 60 \text{ s/min}} \\ &= 12 \text{ C/s} = 12 \text{ A} \end{aligned}$$

The average current was 12 A.

## ELECTROCHEMISTRY

## ELECTROLYSIS CALCULATION

1. Determine the mass of magnesium deposited at the cathode of a molten  $\text{MgCl}_2$  electrolytic cell if 10.0 A flow through the cell for 9.65 h.
2. An electroplating firm wishes to plate 12.7 g of copper onto a pair of baby shoes from a  $\text{Cu}(\text{NO}_3)_2$  solution. If a 2.00 A current is used, calculate the time required. At which electrode would the shoes be attached?
3. If 76 g of fluorine are required, what current would have to flow for 10 h to produce the fluorine from molten NaF. At which electrode would this reaction occur?

## ELECTROLYSIS CALCULATION

4. Calculate the current required to plate out 29.35 g of nickel from an aqueous solution of nickel(II) sulfate if the current runs for 10.0 h.
5. How long would a 30.0 A current have to flow to plate out 75.0 g of calcium metal? At which electrode would the reaction occur?
6. If a current plates out 13.5 g of aluminum, what mass of magnesium would be plated out in the same time by the same current?



## ELECTRICAL UNITS

The formulas for calculation of electrical energy in joules and in kilowatt hours are derived below. These formulas appear on the ALCHEM 30 data sheet.

Potential Difference (V)

*Potential difference* refers to the electrical potential energy difference per unit charge between two points in a circuit. It is measured in volts (V). 1 volt = 1 joule/coulomb or 1 V = 1 J/C.

In symbols,

$$\text{potential difference in volts} \quad V = \frac{E}{Q} \quad \text{energy change in joules} \\ \text{charge in coulombs}$$

A useful conversion is, 1 volt = 96.5 kJ/mol  $e^-$ .

Energy (E)

Energy from electrical sources can be calculated from the voltage of the cell and the quantity of charge passed through the source. The SI unit for all energy is the joule (J), but the kilowatt hour (kW·h) is still widely used for measuring energy from electrical sources. Electrical energy in joules can be calculated from the following equations.

$$E = VQ \quad (\text{Since } V = \frac{E}{Q})$$

$$E = VIt \quad (\text{Since } Q = It)$$

energy in joules    potential difference in volts    current in amperes    time in seconds

Electrical energy in kilowatt hours can be calculated using the equation:

$$E = \frac{VIt}{1000}$$

energy in kilowatt hours    potential difference in volts    current in amperes    time in hours

Example:

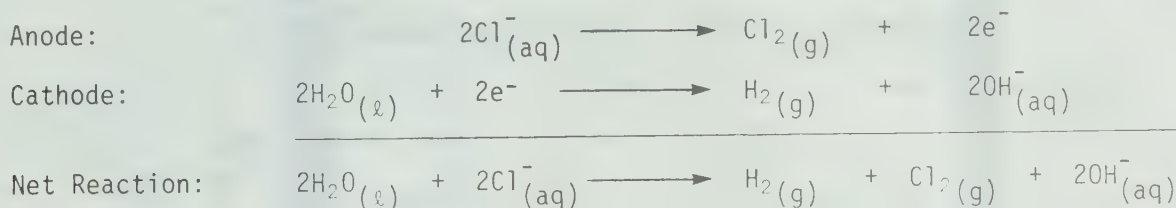
Determine the number of kilowatt hours of electrical energy consumed in an electrolytic cell operated at 2.00 V and 0.25 A for 4.00 h.

$$\begin{aligned} E &= \frac{VIt}{1000} \\ &= \frac{2.00 \text{ V} \times 0.25 \text{ A} \times 4.00 \text{ h}}{1000 \text{ W/kW}} \\ &= 2.0 \times 10^{-3} \text{ kW}\cdot\text{h} \end{aligned}$$

Since 1 V·A = 1W,

## CHLOR-ALKALI ELECTROLYTIC CELLS

The Dow Chemical complex at Fort Saskatchewan (about 15 km north-east of Edmonton) contains the only chlor-alkali plant in Alberta. The Fort Saskatchewan site was chosen because of the large salt beds underneath the area. The salt is pumped from the ground by forcing high pressure steam into the salt beds below. The basic chemistry of the plant involves the continuous electrolysis of aqueous sodium chloride.



The hydrogen gas produced is reacted with chlorine gas to produce hydrogen chloride gas and subsequently  $\text{HCl}_{(\text{aq})}$ , muriatic acid. The remaining hydrogen gas is released into the atmosphere.

The chlorine gas is purified by being cooled and compressed into a liquid state. The liquid chlorine is then used to produce bleaches (e.g., calcium and sodium hypochlorite), plastics (e.g., polyvinylchloride, PVC), pesticides (e.g., 2,4-D), and solvents (e.g., 1,1,2,2-tetrachloroethene). Most of the chlorine produced at Fort Saskatchewan is used as a chlorine bleach by Alberta's pulp and paper industry.

The residual electrolyte from the electrolysis is aqueous sodium hydroxide. The sodium hydroxide solution is concentrated by evaporation and sold as caustic soda (primarily to the pulp and paper industry).

Questions:

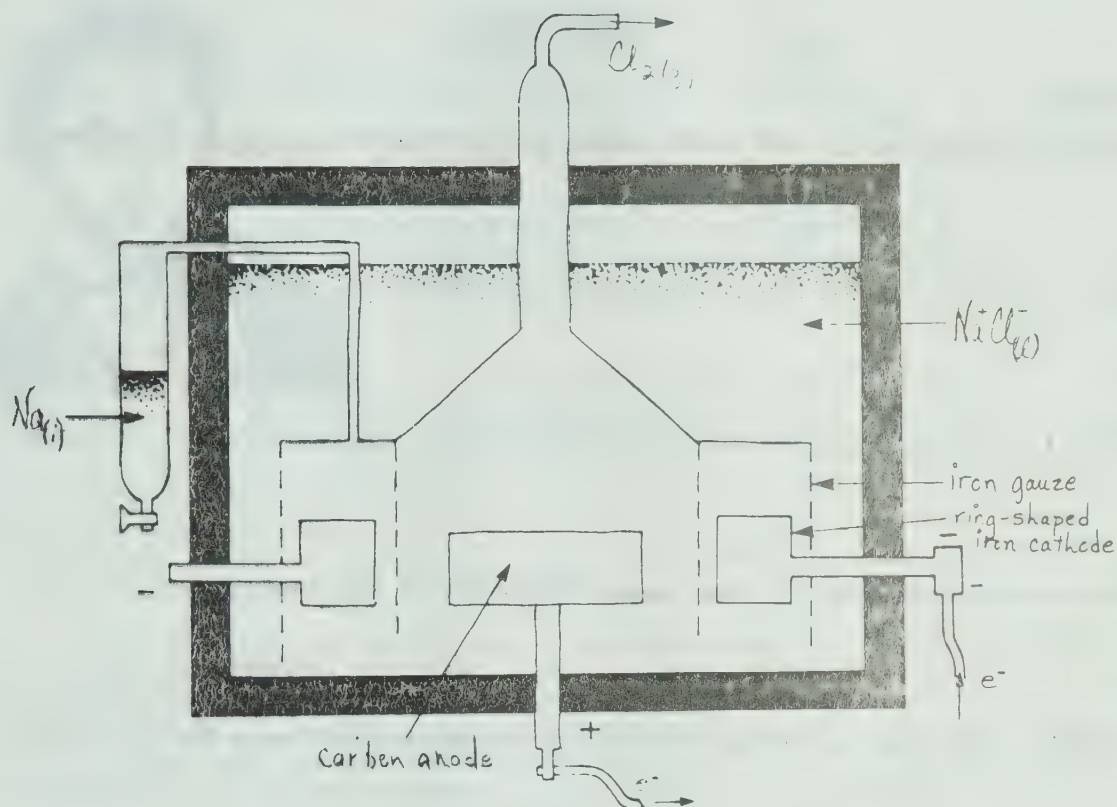
1. Write in the  $E^\circ$  values beside the equations above and determine the minimum *theoretical* voltage required to operate a single cell. (The *actual* voltage applied is 3.1 V.)
2. What mass in tonnes (1000 kg) of sodium chloride is consumed in one cell (of the two hundred at Dow Chemical) when a current of  $5.50 \times 10^4 \text{ A}$  flows for 24.0 h?

# CHLOR-ALKALI ELECTROLYTIC CELLS

3. If all the chlorine gas produced in 24.0 h were used to fill laboratory demonstration tanks at 65.0 mol per tank, how many tanks could be filled?
4. What would be the total cost of operating one cell for 24.0 h if the cost per kilowatt hour is 0.8¢? Determine the cost for 200 cells for 24.0 h.
5. An electrode requires about  $0.800 \text{ A/cm}^2$  to operate efficiently. Determine the approximate area of the electrodes in the cell above.



## DOWNS PROCESS



Downs Cell

Figure M11

Downs Process

In the Downs process a direct current of electricity is passed through molten sodium chloride to liberate sodium metal and chlorine gas. Current can flow through molten  $\text{NaCl}$  because molten  $\text{NaCl}$  exists as separate  $\text{Na}^+$  and  $\text{Cl}^-$  ions. At the ring-shaped cathode the sodium ions are reduced and at the central carbon anode the chlorine ions are oxidized. Sodium, being lighter than the molten salt, rises and overflows into a separate container, and the chlorine collects in the specially designed compartment above the anode. Sodium chloride melts at  $805^\circ\text{C}$  but calcium chloride is added to the sodium chloride to reduce the melting point.

A check of the Canadian Chemical Register indicates that sodium metal is not produced on a commercial scale anywhere in Canada (i.e., there are no commercial Downs Cells in Canada). Chlorine is produced in over a dozen places in Canada including Dow Chemical's chlor-alkali plant at Fort Saskatchewan, Alberta.

## ELECTROCHEMISTRY

### DOWNS PROCESS

#### Questions:

1. Write the equation for the simultaneous melting and dissociation of sodium chloride.
2. Write the equation for the cathode half reaction in the Downs Cell.
3. Write the equation for the anode half reaction in the Downs Cell.
4. Write the net equation for the overall reaction in the Downs Cell.
5. Determine the time to produce 1.00 mol of chlorine gas from a 40.0 A current.
6. If the voltage used was 5.00 V, determine the number of kilowatt hours of energy used.
7. A 5 kg bottle of chlorine contains about 70 mol of chlorine gas. What would the electricity to produce the chlorine cost at 1.0¢/kW·h?

## ELECTROCHEMISTRY

## SIR HUMPHRY DAVY

Sir Humphry Davy (1778-1829)

Davy, the eldest son of a wood carver, was born in Penzance, England on December 17, 1778. When Davy was sixteen his father died and he was forced to quit school and go to work. Although his main interest was poetry, he was apprenticed to an apothecary, a person licensed to prescribe and sell drugs and medicines. He was discharged from his first position when some of his private experiments resulted in explosions.

At the age of eighteen Davy read Lavoisier's book, *Elementary Treatise on Chemistry*, and became very interested in the subject. He completed his apprenticeship and became the superintendent of an institution for the study of the therapeutic properties of gases. While studying gases he discovered the anesthetic properties of laughing gas ( $N_2O$ ). At the age of 23 he became a lecturer at the newly founded Royal Institution in London. His lectures, based on his work in chemistry, became widely popular and 11 years later he was knighted. At the age of 41 he became president of the Royal Society.

Davy's most important scientific work was with electricity. He constructed a battery with over 250 metallic plates and used it to pass electricity through aqueous solutions and molten compounds. In 1807 he was successful in liberating potassium metal from molten caustic potash (KOH). A week later he used the same procedure to liberate sodium metal from molten caustic soda (NaOH). He also isolated for the first time the elements; barium, strontium, calcium and magnesium. He narrowly missed being the first to isolate boron. Davy proved that chlorine is an element and not a compound as previously thought.

Davy attempted to use electricity for illumination by making the first arc lamp. He was also the first person to note the catalytic ability of platinum.

Davy's later life was marred by poor health, probably caused by prolonged close contact with poisonous chemicals. He spent his last years traveling in Europe seeking better health. He died in Geneva, Switzerland, on May 29, 1829.



## ELECTROCHEMISTRY

## AN OVERVIEW - QUALITATIVE ASPECTS

In an experiment similar to Lab M1 the oxidizing strengths of five heavy metal ions was studied. The results of the experiment are shown in the table below. A check mark indicates that a reaction occurs and a dash indicates that no reaction occurs. The concentration of all the metal ions was 1.00 M.

Species Metal in Strips solution	$\text{Bi}^{3+}_{(\text{aq})}$	$\text{Au}^{3+}_{(\text{aq})}$	$\text{Pb}^{2+}_{(\text{aq})}$	$\text{Hg}^{2+}_{(\text{aq})}$	$\text{Tl}^{+}_{(\text{aq})}$
bismuth, $\text{Bi}_{(\text{s})}$	—	✓	—	✓	—
gold, $\text{Au}_{(\text{s})}$	—	—	—	—	—
lead, $\text{Pb}_{(\text{s})}$	✓	✓	—	✓	—
mercury, $\text{Hg}_{(\text{s})}$	—	✓	—	—	—
thallium, $\text{Tl}_{(\text{s})}$	✓	✓	✓	✓	—

1. Make a reduction potential table for the metal ions. Place the strongest oxidizing agent at the top of the table.

2. Which of the metals would likely produce  $\text{H}_2$  gas when placed in a 1.00 M solution of  $\text{HCl}_{(\text{aq})}$ ?

## AN OVERVIEW - QUALITATIVE ASPECTS

For each of the following situations predict the most likely redox reaction, write a balanced net ionic equation for the predicted reaction and indicate whether or not the reaction is spontaneous.

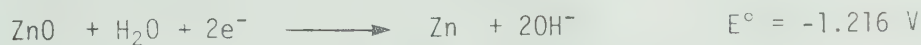
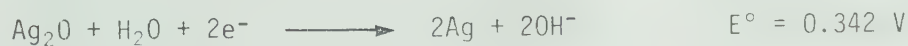
1. Chlorine gas is bubbled through an aqueous solution of sodium iodide.
2. An iron nail is placed in an aqueous solution of stannous chloride.
3. Electricity is passed through an aqueous solution of aluminum sulfate.
4. An acidic solution of aqueous potassium permanganate stands for several days in a closed bottle.

ELECTROCHEMISTRY  
AN OVERVIEW - QUALITATIVE ASPECTS

5. An acidic solution of tin(II) chloride is titrated with aqueous potassium dichromate.
6. A strip of silver is placed in aqueous copper(II) sulfate solution.
7. Copper roofing material is exposed to moist air.
8. Electricity is passed through an aqueous solution containing sodium chloride, potassium bromide, and lithium iodide.
9. A small piece of sodium metal is dropped into a beaker of water.

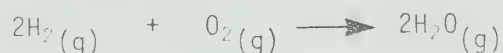
## AN OVERVIEW - QUALITATIVE ASPECTS

The equations involved in the operation of a silver-zinc cell are given below along with their reduction potentials. Use the equations to answer the questions which follow.



1. Write and label the anode and cathode half reactions, the net ionic equation. Include the  $E^\circ$  values and the physical state of each species.

2. The hydrogen fuel cell employs hydrogen and oxygen gas as fuels. The net reaction is:



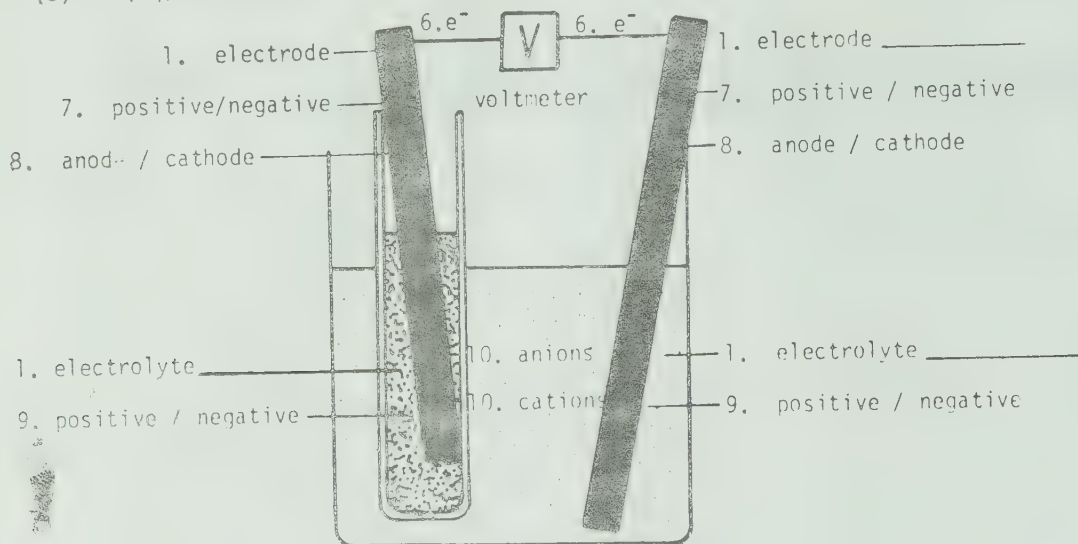
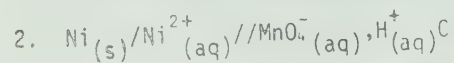
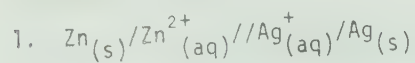
Propose half reactions and an  $E^\circ_{\text{net}}$  for the  $\text{H}_2$ - $\text{O}_2$  fuel cell. (Bonus: Compare the  $E^\circ_{\text{net}}$  with the  $\Delta H$  for this reaction.)



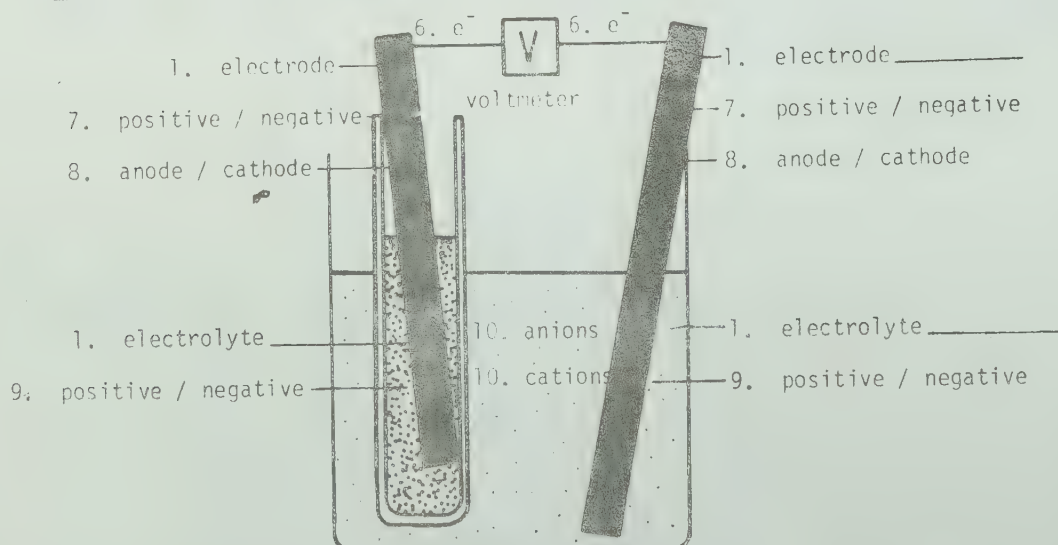
## ELECTROCHEMISTRY

## AN OVERVIEW - QUALITATIVE ASPECTS

Use the electrochemical cell answer blanks to provide a complete analysis of the following electrochemical cells.



2. reduction half reaction:
3. oxidation half reaction:
4. net reaction:
- \* 5. spontaneous: YES / NO



2. reduction half reaction:
3. oxidation half reaction:
4. net reaction:
5. spontaneous: YES / NO

## ELECTROCHEMISTRY

## AN OVERVIEW - QUANTITATIVE ASPECTS

1. 20.0 ml of  $\text{Cr}_2\text{O}_7^{2-}$  solution is titrated with 40.0 ml of 0.100 M  $\text{Fe}^{2+}$  solution. Calculate the molar concentration of  $\text{Cr}_2\text{O}_7^{2-}$  in solution.

2. The following data was obtained from titration of 25.0 ml of 0.200 M  $\text{SnCl}_2$  aqueous solution with  $\text{KMnO}_4$  aqueous solution.

	<u>Trial 1</u>	<u>Trial 2</u>
final buret reading	20.41 ml	40.62 ml
initial buret reading	<u>0.22 ml</u>	<u>20.41 ml</u>
volume of $\text{KMnO}_4$ used		

Calculate the molar concentration of the  $\text{KMnO}_4$  solution.

3. In an analysis to determine the concentration of commercial hydrogen peroxide, 10.0 ml of  $\text{H}_2\text{O}_2$  were pipetted into a flask. After the solution was acidified it was titrated with 0.100 M  $\text{KMnO}_4$ . When 42.50 ml of  $\text{KMnO}_4$  were added, the solution turned a faint persistent pink. What is the concentration of the  $\text{H}_2\text{O}_2$  in the commercial hydrogen peroxide?

## ELECTROCHEMISTRY

### AN OVERVIEW - QUANTITATIVE ASPECTS

The elements sodium, potassium, magnesium, calcium, strontium, and barium were first isolated by the English scientist, Sir Humphry Davy. During the period from 1807-1808 Davy produced these metals by electrolysis of their molten compounds. If Davy used 2.00 A of current for 1.00 h, how much metal would be produced in each of the following cases?

4. Electrolysis of molten caustic potash (potassium hydroxide).

*(The oxidation of  $\text{OH}^-_{(l)}$  yields the same products as the oxidation of  $\text{OH}^-_{(aq)}$ )*

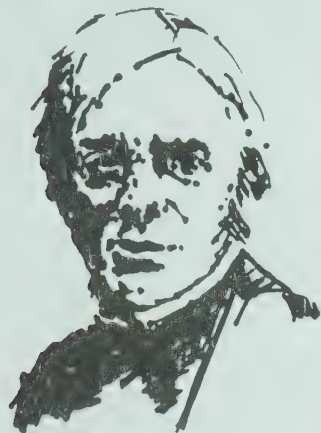
5. Electrolysis of molten caustic soda (sodium hydroxide).

6. Electrolysis of molten magnesia (magnesium oxide).

## ELECTROCHEMISTRY

### AN OVERVIEW - QUANTITATIVE ASPECTS

7. An English scientist named Michael Faraday (who began his scientific career as Humphrey Davy's lab assistant) did extensive work on the electrolysis of aqueous solutions. In one experiment he passed electricity through three electrolytic cells joined in series. The cells contained aqueous solutions of  $\text{AgNO}_3$ ,  $\text{Cr}(\text{NO}_3)_2$ , and  $\text{Pb}(\text{NO}_3)_2$ . If 10.8 g of silver were produced in the experiment what mass of chromium and lead were also produced? (*For cells in series, the same current will pass through each cell.*)



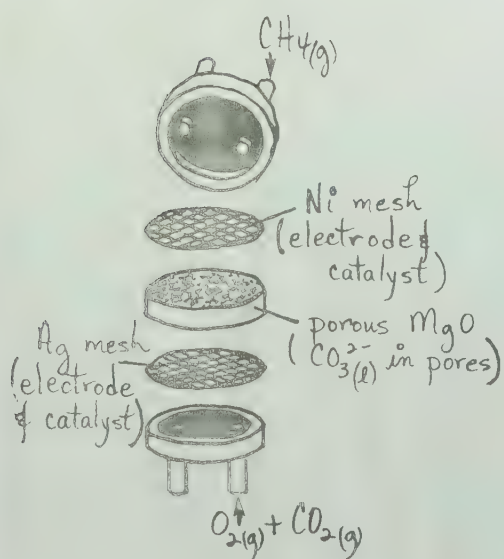
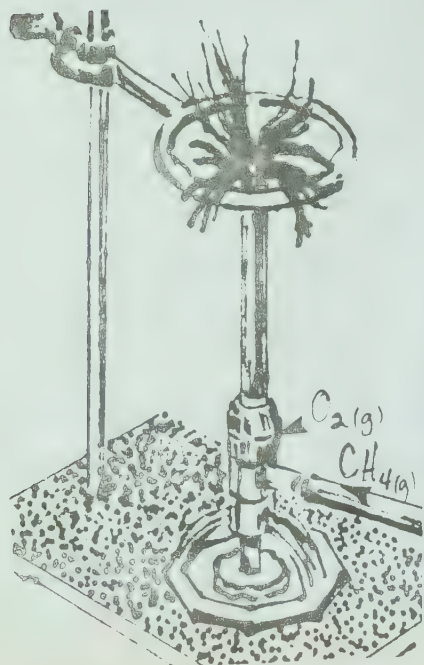
"Davy's Greatest Discovery"  
Michael Faraday



## ELECTROCHEMISTRY

## AN OVERVIEW - QUANTITATIVE ASPECTS

8. Calculate the amount of energy released when 100 g of methane burns in a bunsen burner or furnace, and then calculate the amount of energy released when 100 g of methane is reacted in a  $\text{CH}_4\text{-O}_2$  fuel cell (see earlier half reactions). Which reaction produces more energy?



$\text{CH}_4\text{-O}_2$  Fuel Cell  
(operates at  $580^\circ\text{C}$ )









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